RUBBER CHEMISTRY AND TECHNOLOGY

VOLUME XVIII NUMBER 4

October, 1945

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of the
AMERICAN CHEMICAL SOCIETY

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Published quarterly under the Auspices of the Division of Rubber Chemistry
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Lancaster, Pa.

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RUBBER CHEMISTRY AND TECHNOLOGY

RUBBER CHEMISTRY AND TECHNOLOGY is published quarterly under the supervision of the Editor representing the Division of Rubber Chemistry of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

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AN INVITATION FROM POSTWAR BRITAIN

The Secretary of the Division of Rubber Chemistry has received a letter from the Institution of the Rubber Industry, in which the latter, in its ever cordial spirit, invites our members to present papers at some of its future meetings. It will be remembered that, before the War, papers were presented by Rubber Division members at meetings of the Institution, where our members were always given the warmest of welcomes and came away with a lasting feeling of good will and comradeship.

There could be no better time than the present for renewed coöperation and fellowship between our two organizations, and so there seems to be every reason to accept, both in spirit and in deed, this generous invitation. It is to be hoped that some of our members will, in the not too distant future, be in a position to take part in meetings of the Institution.

THE INSTITUTION OF THE RUBBER INDUSTRY

12 Whitehall, London, S.W. 1,
June 14, 1945.

Dr. H. I. Cramer,
Sharples Chemicals, Inc.,
23rd and Westmoreland Sts.,
Philadelphia, Pa.

Dear Sir,

Now that the war in Europe is over, this Institution is anxious to arrange meetings when papers will be given by visitors from the States, as it is felt that these would do much to promote coöperation and understanding between members of the industry in both countries.

I have, therefore, been instructed to ask you to be good enough to make it known to your members that my Papers Committee would welcome papers from any who are visiting this country. If they would advise me of the date of their visit and the subject of their paper, my Committee would be glad to make suitable arrangements.

Your kind coöperation in this matter would be much appreciated, as it is many years since the Institution has had the pleasure of having papers from American visitors.

Yours faithfully,

(Miss) C. CARDEN
Secretary

NEW BOOKS AND OTHER PUBLICATIONS

WARTIME TECHNOLOGICAL DEVELOPMENTS. Prepared by the Department of Labor, Washington, D. C. 6 x 9 in. 418 pp. Available from Superintendent of Documents, Washington 25, D. C., at 50c per copy.—This report, comprising a study of wartime technological developments in the United States, was prepared by the Productivity and Technological Development Division of the Bureau of Labor Statistics for the Subcommittee on War Mobilization of the Senate Committee on Military Affairs. Divided into two parts, it first presents a brief appraisal of the published literature on wartime technological developments and then digests some of the more significant excerpts from this literature for 1942 and 1943. A digest for the year of 1944 is now in preparation and will be issued as a supplement to the present report in the near future. All types of materials and all kinds of processes are covered in the report, a good number of them of direct interest to the rubber manufacturing industry, most of which were digested from the various rubber journals. A detailed cross-reference index is included. [From *The Rubber Age* of New York.]

SYNTHETIC RUBBER MECHANICAL PARTS IN PRESENT AND POSTWAR VEHICLES. By Ellwood F. Riesing. Published by Firestone Industrial Products Co., Akron, Ohio. 8½ x 11 in. 32 pp.—This is a reproduction of a paper which the author, chief automotive engineer of the company, presented at the War Engineering-Annual Meeting of the Society of Automotive Engineers, held in Detroit, Mich., January 8–12. The booklet discusses the present and potential use of synthetic rubber in mechanical parts with respect to efficiency, low-temperature flexing properties, resistance to ultraviolet rays, ozone, acid, and gas diffusion, electrical resistivity, hysteretic and elastic properties, creep and stress relaxation under load at elevated temperatures, and change in modulus with time at elevated temperatures. Included are studies of operating temperatures and tension modulus at operating temperatures and of static compression and shear modulus, and dynamic compression and shear modulus, at low frequencies (free vibration). Synthetic rubberlike elastomers as future engineering materials are also discussed. The booklet is illustrated with graphs, statistical tables, and photographs, and is accompanied by a bibliography and a glossary of rubber chemical and engineering terms. [From *The Rubber Age* of New York.]

GENERAL SALES AND DISTRIBUTION CIRCULAR—NATURAL AND SYNTHETIC RUBBER. July 1, 1945. Reconstruction Finance Corp., Office of Rubber Reserve, Washington, D. C. 28 pages.—As explained in the introduction, this circular sets forth the procedure for the sale and distribution by Reconstruction Finance Corp., Office of Rubber Reserve, of natural and synthetic rubber and supersedes all previous circulars issued by the Rubber Reserve Co. It is pointed out that as used in this Circular, the term "Rubber Reserve" means Reconstruction Finance Corp., Office of Rubber Reserve, 811 Vermont Ave., N.W., Washington, D. C. [From the *India Rubber World.*]

LE CAOUTCHOUC D'HEVEA. Initiation aux Méthodes d'Exploitation en Indochine. (Hevea Rubber. Introduction to Methods of Cultivating it in Indo-China.) Institut Français du Caoutchouc. Paris: 1945, pp. 159 + 74 plates. Price, 400 francs.—This book was examined with special interest as one of the first French textbooks to be received in this country since 1940. While the paper is of wartime quality, adversely affecting the clarity of a few of the many photographic reproductions, the type is exceptionally clear and the matter well spaced.

The book is a concise but comprehensive practical manual of instruction, written for the young planter, the young botanist, or the young agronomist, who has no precise knowledge of the specialized field of rubber planting. It is the result of direct collaboration between the planters and the Institut Français du Caoutchouc. An introductory section by J. le Conte deals with Hevea brasiliensis and other rubber-producing plants, development of the plantation industry, and botanical aspects of latex. The main part, by H. Regnauld, is devoted to methods of exploiting rubber, first from the forests of the Amazon and Africa and secondly from the plantations. The plantation section gives practical details, with many illustrations, relating to the establishment of a plantation, reproduction of trees by budding, soil conservation, diseases and pests of the rubber tree, methods of tapping, collection of latex, and the preparation of smoked sheet, crepe rubber, concentrated latex, and powdered rubber. The flatter nature of the country in Indo-China, compared with Malaya, tends towards larger plantations. Consequently, estate factories are on a somewhat larger scale than in Malaya, and this fact is brought out in the book. The third and last part of the book, written by G. Colin, gives a brief summary of the properties of crude and vulcanized rubber and of compounding, processing, and vulcanizing. Reclaim, ebonite, rubber derivatives, and the manufacture of goods from latex are touched upon. A short list is appended of French technical books and journal articles. The absence of a subject index somewhat detracts from the value of what is otherwise a most useful and timely publication. [From the *Journal of Rubber Research.*]

EXPERIMENTS WITH RUBBER IN MEXICO. By S. K. Lowe and Maurice Ries. Published by the Middle American Research Institute of the Tulane University of Louisiana, New Orleans, La. 7¾ x 10¾ in. 114 pp.—Based on the discovery of an old Spanish manuscript covering experiments made between 1785 and 1798, and published with the coöperation of the Firestone Tire & Rubber Co., this document reveals that rubberized textiles had been in use for some time before 1785, and accordingly pushes back the acknowledged date for the first extensive commercial use of rubber about forty years. The discovered manuscript, translated by S. K. Lowe, indicates that a series of experiments were ordered by the Viceroy of Mexico in an effort to find a leakproof container for the shipment of quicksilver. The entire manuscript is reproduced in the current document, along with an extensive introduction by the authors. [From *The Rubber Age* of New York.]

SOUTH AMERICAN LEAF BLIGHT OF HEVEA RUBBER TREES. Technical Bulletin No. 882. January 1945. United States Department of Agriculture, Washington, D. C. 32 pages.—The Para rubber tree, *Hevea brasiliensis*, is adaptable to the soil and climate of vast areas in Mexico, Central America, and South America, but, despite factors favoring a rubber growing industry in tropical America, most early *Hevea* rubber growing enterprises there ended

in failure. The devastating attacks of the South American leaf blight caused by the fungus *Dothidella ulei* has been one of the unfavorable biological factors. This booklet, supplementary to Circular No. 686 of the Department of Agriculture, "Fungicidal Control of South American Leaf Blight of *Hevea* Rubber Trees", describes a coöperative rubber planting program, a blight control program, distribution, damage, fungus, host, and environment. Photographs of the leaf blight conidia and leaf blight ascospores in water in the ungerminated and in the germinated stages are included. A table shows the relation of length of incubation period to the number of lesions incited on young *Hevea* seedlings inoculated with conidia of *Dothidella ulei*. At an incubation period of eight hours, there is approximately one lesion per leaf, but as the incubation period increases, there is a very sharp increase in the lesions per leaf. This bulletin is in effect also a supplement to a 1942 article in *India Rubber World*, titled "*Hevea* Rubber Culture in Latin America" and written by R. D. Rands, Special Rubber Investigations, Bureau of Plant Industry, United States Department of Agriculture. [From the *India Rubber World*.]

1945 Yearbook of The Los Angeles Rubber Group, Inc. The Los Angeles Rubber Group, Inc., Hotel Mayfair, Los Angeles, Calif. 48 pages.—This year's edition of the Yearbook contains twice as many pages as the 1944 edition, and some of these extra pages are devoted to a more detailed report on the regular and special meetings of the Group held during the past year. Special features include an article on "The Rubber Industry of Los Angeles", by James F. Bone, and sections on classification and general properties of commercial synthetic rubbers produced in U. S. A.; effect of softeners on GR-S compounds; carbon black nomenclature; and formulas for basic general classes of accelerators. As usual, an up-to-date list of Pacific Coast rubber manufacturers and suppliers to the rubber industry, arranged geographically and alphabetically, is contained in this booklet. A list of the members and the latest by-laws of the Group complete this edition of the book. [From the *India Rubber World*.]

South America Called Them. By Victor Wolfgang von Hagen. Published by Alfred A. Knopf, 501 Madison Ave., New York, N. Y. 5¾ x 8½ in. 311 pp. $3.75.—This is a well-told story of four scientists—La Condamine, Humboldt, Darwin and Spruce—whose explorations in South America, spread over a century and a half, and unlocked the riches of that continent, including rubber. The whole story of South America is found in the book—the giant peaks of the Andes, the torturous path of the Amazon, the rain-sodden plains of the Orinoco, the nitrate deserts of Chile and Peru, the iron-mountained island of Tierra del Fuego. Well-written by an explorer who has traveled over much of the territory opened up by the earlier scientists, the book combines sound science and factual history.

Although Charles-Marie de La Condamine, who was sent to South America by the French Académie des Sciences to help determine the true shape of the earth, in an effort to disprove the Newtonian theory, was not the first to see rubber, since Columbus had reported its existence and Cortez found the Aztecs playing the game of *tlachti* with solid rubber balls, his reports were the first to attract Europe's attention to rubber and, according to this book, "his were the first scientific experiments, his the first mention of the Hevea tree" and "he was the first to bring back samples of rubber to Europe". La Condamine's first contact with rubber came in 1736 in the Esmeraldas area, when the

natives brought him a piece of stretching "cloth" which they called *caoutchouc*. Recognizing the water-resistant properties of the material, La Condamine "fashioned himself a rubber pouch for his quadrant", and thus unknowingly became the first white rubber manufacturer.

Before returning to France to report on his findings to the Académie des Sciences, La Condamine traveled the entire length of the mighty Amazon, from west to east. He continued to investigate the rubber plant during this trip and noted the existence of rubber trees along the entire length of the Amazon basin. He noted the use of moulds by the natives, and gathered syringes and "pumps which the Indians made of rubber, which among the Omaguas are a very common utensil". These he brought to Europe, along with chunks of coagulated rubber, and, according to the author, "so began the history of that product (rubber) which changed the industry of the world". Back in France, La Condamine "wrote of rubber, he experimented with the samples that he had brought back, he introduced it for the first time to the scientists of Europe".

Although La Condamine's connection with the early discoveries of rubber are fairly well known to the modern rubber industry, it is not generally known that he is also credited with the discovery of platinum and rotenone. During his South American venture some of the sambos in his party picked up metal which, being neither gold nor silver, was called *platina*. When finally examined by metallurgists in Europe, it became known that La Condamine had discovered platinum. When he found the natives using "leaves or roots which when thrown into the water have the faculty of intoxicating fish", he collected the plant and became the European discoverer of *varvascu*, or barbasco, which contains the alkaloid known as rotenone, now widely used as an insecticide.

Of the other three scientists, Humboldt and Darwin paid little attention to rubber during their respective work in South America, but Richard Spruce, one of the greatest botanical explorers in history, witnessed the growth of Belem, Para and Manoas into tremendous rubber centers. Returning from the heart of the jungles to Manaos in 1854 he found himself in the midst of the first large rubber boom, with the price of rubber already exceeding the $1.50-a-pound mark. Some of the plants and specimens of rubber products which Spruce had sent to the outer world were in part responsible for this boom. In some of his reports Spruce also told of watching the *seringueros* tapping Hevea trees "with a series of deep chevrons cut into the bark".

This book should prove of interest to the rubber industry because of its historical value and because it tells so well the story of South America, which, once again, is an important producer of rubber. It is well documented and contains a carefully-prepared index. [From *The Rubber Age* of New York.]

A Borracha no Brasil. First Series. Amando Mendes. Sociedade Impressora Brasileira, Brusco & Cia., Sao Paulo, Brazil, 1943. Paper, 5 by 7½ inches, 200 pages. Tables. Illustrations. Second Series. Amando Mendes. Editoria Difusao S/A., Sao Paulo, Brazil, 1943. Paper, 5 by 7½ inches, 196 pages. Tables.—Amando Mendes, well known to his countrymen as a specialist in rubber, began to devote himself to the subject in 1939. In the above two volumes he has collected a number of studies on various aspects of the rubber industry, written mainly with the aim of spurring Brazilians on to insure future supplies of raw material for the country's expanding rubber manufacturing industry by giving serious attention to the growing of rubber in

Brazil. In some of the articles he discusses the world position of rubber, the present situation and future prospects; in others he gives suggestions on where and how to start plantations, and examines the economics of the business, both from the point of view of the rubber collector and the contractor or owner. Mendes believes that the best procedure in Brazil is to plant alternate rows of *Hevea brasiliensis* and *Manicoba* (*Manihot glaziovii* and *Manihot dichotoma*) five meters apart with, between the rows, catch-crops like almonds, soya beans, even rice, cotton or other annual, low-growing crops. He recommends *Manicoba* along with *Hevea* because, as he explains, although the yields are lower and the rubber, while serviceable, is inferior to that from *Hevea*, the tree grows faster than *Hevea*, and can be tapped in two or three years, thus providing supplies of rubber while *Hevea* is developing. Furthermore *Manicoba* has the advantage of being resistant to most of the diseases—if not all—that afflict *Hevea*.

Much of the same ground is covered in both books; but older material in the first series is brought up-to-date in the second. It is a pity, however, that when treating—in the first part—early estate practice in the Far East, particularly tapping methods. Mendes did not make it sufficiently clear that the procedures were outmoded and that recent methods were presented in the later series. [From the *India Rubber World*.]

THE LIFE OF A TIRE.—Goodyear Tire & Rubber Co., Akron, O. 30 pages. —This profusely illustrated booklet was prepared for the explanation of tire conditions and their causes. Descriptions and illustrations are given of the more common conditions which reduce tire wear. Also discussed are fabric breaks, cuts, tread and irregular wear, overload, heat injuries, matching dual tires, and wide rims. Of particular value to truck and bus operators is the section covering the use of wide rims. It is emphasized that wide rims develop greater stability, which produces the following improvements: reduces rate of tread wear due to decrease in tread scuffing and increased tread contact area; reduces tread-cracking, strain in the tire bead, and flex strain on rims; and produces straighter sidewalls. Covered in the chart section are: effect of inflation on tire performance under normal conditions, effect of load on tire performance, effect of temperature on tread wear, effect of date of application of tire performance, effect of wheel position on tire performance, effect of rotation of tires on tread wear, effect of type of roads of tire performance, and bleeding and tire temperature. [From the *India Rubber World*.]

SYNTHETIC RUBBER FROM ALCOHOL. By Anselm Talalay and Michael Magat. Published by Interscience Publishers, Inc., 215 Fourth Ave., New York 3, N. Y. 6 x 9 in. 298 pp. $5.00.—As stated on the title page, this book is "A Survey Based on the Russian Literature". It is just that, with a small proportion based on references to American, British and German journals and patents. The greater proportion of the references to the Russian literature are earlier than 1935. The reviewer knows no Russian, but it looks as if the authors have done this work well, making available to American readers significant work published in Russian.

The Russian synthetic rubber is almost entirely sodium-polymerized butadiene. Apparently only a small amount is formed by emulsion polymerization, "Whenever the latex can be used directly" (p. 124). The butadiene is prepared by Lebedev's method from alcohol. Ostromislensky in 1915 suggested making butadiene from a mixture of alcohol and acetaldehyde but it proved

to be "industrially unsuccessful". It became, however, "the forerunner of the Carbide and Carbon process, upon which the tremendous 'butadiene-from-alcohol' program has largely been based in the United States". (p. 1.) Nothing further is given about this process.

The book contains four chapters: (I) The Lebedev Process, (II) Technology of the S. K. Process, (III) Polymerization, and (IV) Physiochemical Properties of the Polymers. The first two chapters were written mainly by A. Talalay and the second two by M. Magat. The first two cover 90 pages and the second two 195 pages. Some of the headings of subsections are: Chemistry of the Process, Factors Influencing the Lebedev Catalysts, Pilot and Industrial Installations, Homogeneous and Catalyzed Thermopolymerization, Emulsion Polymerization, Sodium Polycondensation, Technology of Sodium Polymerization, General Properties and Structure of the Polymer, Effects of Chemical and Physical Agents on the Solid Polymer and in Solution, and Properties of Solutions and Cements.

The book is well written, and contains a considerable amount of technologic and scientific information. Unfortunately, the history of the synthetic rubbers used in many of the experiments and tests is not recorded. The authors discuss at length Ziegler's theory of the formation of a sodium compound with butadiene and conclude that "the process is a polycondensation rather than a polymerization". Sodium was used by the Germans also, but they abandoned it "in favor of the emulsion polymerization, because the latter is now suitable for the production of butadiene-styrene copolymers, Buna-S, and also because they apparently failed to overcome the difficulties arising from overheating".

The authors state, "The economic efficiency of the Lebedev catalysis for making butadiene from ethanol depends in no small measure upon the efficient utilization of the liquid and gaseous byproducts formed. It has been variously estimated that one ton of useful byproduct can be produced for each ton of S.K." There is very little mention of vulcanization and practical properties of vulcanizates. The Russians, like others, have had considerable difficulty with the lack of building-tack in their synthetic rubber.

The book is well printed and apparently free of typographical errors. It is rather unfortunate, however, that the reader is confronted with an error in statement and inference on the very first page where "butadiene-2, 3" is confused with "butadiene-1, 3". The abbreviation, "S.K.", which are the first letters of the Russian words for synthetic rubber, is used without any explanation as to its meaning and derivation. There are excellent author and subject indexes. [Harry L. Fisher in *The Rubber Age* of New York.]

COLLOID CHEMISTRY. Volume V. Edited by Jerome Alexander. Published by Reinhold Publishing Corp., 330 W. 42nd St., New York, N. Y. Cloth, 6 by 9 inches. 1262 pages. Price $20.—This new volume brings up to date the theories, methods, and procedures of colloid chemistry, as previously discussed in the first four volumes of this series. Volume V deals with theory and methods, and biology and medicine; while Volume VI, to follow, will deal with technological applications.

These books should prove of use to scientists in a wide variety of different fields in attacking ever-recurrent problems. In the first part of this Volume V is found the most recent knowledge on surface films by William D. Harkins, on soaps by James W. McBain, on the electron microscope by Albert F. Prebus, on polymerization by H. Mark, on the elasticity of rubber and rubberlike materials by Eugene Guth, and on the measurement of surface areas of finely

divided materials by low-temperature adsorption isotherms by P. H. Emmett; to mention only a few.

The second part of Volume V, devoted to biology and medicine, discusses subjects of interest to all scientists, no matter what their special field may be. Chapters on catalysis in biology by Jerome Alexander, photosynthesis by Paul Rothemund, plant cell membranes by Wanda K. Farr, immunology by William C. Boyd, gerontology by A. J. Carlson, infective aerosols by M. W. Jennison, and the action of war gases by Chauncey D. Leake and David F. Marsh, are of special interest.

The chapter by Harkins, in addition to including material on the development and use of the film balance, concludes with comment on the adsorption isotherm method of determining the area of finely divided solids such as carbon black. The emphasis in the chapter by McBain is on soapless detergents and evidence of many sizes and kinds of colloidal particles in a given suspension, these sizes and kinds shifting according to concentration. The chapter on the electron microscope by Prebus includes a discussion of studies of colloidal carbon by the Columbian Carbon Co. research laboratories. Polymerization, as discussed by H. Mark, summarizes the part played by activation processes, the propagation reaction, and the termination reaction in the formation of macromolecules. Rubber elasticity, by Eugene Guth, summarizes recent papers on this subject as delivered by Guth and James during the past few years, as well as the most recent work of other investigators, such as Flory and Fuller. Surface area and particle size measurements on carbon black and zinc oxide are reported in the chapter by P. H. Emmett.

As indicated by the editor, this and future volumes are of value because not only are the data and points of view assembled important in themselves, but the reader is subjected to the influence of knowledge obtained in fields remote from his own; and this has a quickening influence. As usual, complete subject and author indexes are included. [From the *India Rubber World.*]

THE CARBON REËNFORCEMENT OF NEOPRENE-GN. Columbian Carbon Co., 41 East 42nd St., New York 17, N. Y. 5½ x 7¾ in. 88 pp.—Issued as Vol. VI, No. 1, of the "Columbian Colloidal Carbons" series, the studies in this report were designed to trace the trend of properties with colloidal carbon surface. It is divided into five sections, as follows: (1) Comparison with Published Data; (2) Effect of Carbon Loading and Grade on Neoprene-GN; (3) The Three Basic Properties of Carbon and Their Effect on Neoprene-GN; (4) Rubber Property Correlations; (5) Lower Modulus in Neoprene-GN. A bibliography is included. [From *The Rubber Age* of New York.]

DEVELOPMENTS AND STATUS OF CARBON BLACK. Isaac Drogin. United Carbon Co., Inc., Charleston, W. Va. Paper, loose-leaf, 8½ by 11 inches. 126 pages.—As mentioned in the preface by Oscar Nelson, President of United Carbon Co., there have been noteworthy and far-reaching changes in the carbon black industry in the last few years with regard to processes of manufacture, development of new types of carbon black, and the uses of carbon black in both natural and synthetic rubber; and it is timely, therefore, to present the important facts on carbon black and their significance. Developments since February, 1945, when this preface was written, have further increased the value of the information on the present-day carbon black industry and its products.

This well-done publication, which is amply illustrated with photographs

and charts, first presents the prewar and war status of carbon blacks. Tables from Bureau of Mines statistics show production, shipments, prices, and inventories of carbon blacks from 1887 through 1943, and production and shipments for 1944 and 1945 are forecast. The new types of blacks developed for use with synthetic rubber are reviewed in another section, and the demand and supply position and the postwar status of carbon black are discussed with reference to the published statements of leading rubber industry executives on future rubber consumption.

Of special interest is the section on review of manufacturing processes, which describes in detail the channel process and the furnace processes, both combustion and thermal. Extensive technical data are given in sections on processing and reënforcement of blacks in GR-S and smoked sheet. The many physical and chemical tests used in examining carbon black are described, as well as the actual rubber laboratory evaluation methods. Under classification and description of carbon blacks, the trade marked grades of all companies are identified according to the WPB system, and the test characteristics of representative United Carbon and other company blacks are listed. There is in addition an index of rubber grade blacks, a glossary, an index of patents, and a list and map showing the location of carbon black plants in the U. S. [From the *India Rubber World*.]

A.S.T.M. Standards on Rubber Products. Published by the American Society for Testing Materials, 260 So. Broad St., Philadelphia 2, Penna. 6 x 9 in. 532 pp. $2.75.—This latest A.S.T.M. Standards, compiled by Committee D-11 covering rubber products and related materials, includes 75 specifications and tests. Some 160 pages are devoted to general methods of testing rubber products, including chemical analysis, sample preparation for physical testing, tension testing, accelerated aging, state of cure, adhesion, hardness, changes in liquids, and brittleness. Many other properties are covered.

Test methods for specific rubber products, and specifications for them, are compiled together, covering rubber hose and belting; rubber gloves, matting, tape; rubber-coated fabrics; insulated wire and cable; hard rubber and cellular rubber; rubber cements and latices; packing materials; and non-rigid plastics. The book is made complete with the inclusion of several electrical tests and a series of definitions of terms. Several emergency requirements applying to standards for rubber products are given. [From *The Rubber Age* of New York.]

A.S.T.M. Standards: 1944. Published by the American Society for Testing Materials, 260 So. Broad St., Philadelphia 2, Penna. In three parts: Part I—Metals; Part II—Nonmetallic Materials, Constructional; Part III—Nonmetallic Materials, General. Price: $10.00 for any one part; $20.00 for any two parts; $30.00 for all three parts. (For half-leather binding add $1.00 extra for each part.)—Issued in three parts, the complete new 1944 Book of A.S.T.M. Standards contains in their latest approved form all of the Society's widely used specifications and tests for materials. It has 1235 specifications and standard methods and more than 6000 pages. All specifications, whether formal standards or tentative, are given. An innovation in the 1944 Book is the inclusion of all emergency standards and emergency alternate provisions which have been widely used to expedite production and procurement of important materials.

The three parts of the new book follow the previous divisions. Part I covers ferrous metals, nonferrous metals and alloys, and general testing methods. It has 2100 pages and 385 specifications and tests, of which about 225 cover the ferrous metals—steel, cast iron, stainless alloys, etc. Testing methods include metallography, magnesium and magnesium alloys, lead and lead alloys, nickel and nickel alloys, solder and bearing metal, etc. Part II covers constructional nonmetallic materials, such as cement, lime, brick, glass and glass products, concrete, soils and pigments. It has 447 specifications and tests.

Part III, which covers general nonmetallic materials, including rubber products, electrical insulating materials, plastics, naval stores, and textile materials, contains 440 specifications and tests. The section on rubber products covers fire hose, belting, gloves, matting, tape, wire and cable, cements, cellular rubber, hard rubber, synthetics, chemical analysis, tension, accelerated aging, abrasion, adhesions, set, hardness, light checking and dynamic testing. That on plastics covers specifications for phenolics, acrylates, ureas, vinyls, cellulose, etc., and gives tests for impact, mar, water absorption, haze, flammability, shear and tensile strength, effect of heat, etc.

Each part of the 1944 Book has a complete subject index. There are two extensive tables for contents, the first listing all standards under general materials headings and the second being arranged according to the serial designations of the standards. To keep the books up to date, a supplement will be issued to each part late in 1945. These supplements, which may be ordered at the same time the 1944 Book is ordered, sell for $4.00 for any one part, $8.00 for any two parts, and $12.00 for all three parts. Half-leather binding is available at an additional cost of $1.00 for each supplement part.

There are complete indices arranged both numerically and by classification. Supplements are issued in the intervening years and can be ordered at the same time the book is ordered. [From *The Rubber Age* of New York.]

Process Equipment Design. By Herman C. Hesse and J. Henry Rushton. Published by D. Van Nostrand Co., Inc., 250 Fourth Ave., New York 3, N. Y. 6 x 9 in. 580 pp. $7.50.—This is a practical design book, prepared not for the apparatus manufacturer but primarily for the chemical engineer. It presents the fundamentals of mechanics, machine and structural elements, and economic and manufacturing considerations related to the design of process equipment, particularly for the chemical industries. All of the information is well correlated, and from the fundamental facts given the book develops practical methods for the design of the widest range of chemical engineering equipment—pressure vessels, piping, gearing, shafting and bearings, belt and chain drives, attachments and closures, etc. Hundreds of illustrations show minute details and simple formulas are provided for making necessary calculations, with the required data arranged in convenient tables and graphs. Brief references are made to rubber as a lining material and to rubber belts, expansion joints and gaskets. There are 18 chapters, a section of references, and a subject index. [From *The Rubber Age* of New York.]

The Future of Industrial Research. Published by the Standard Oil Development Co., 30 Rockefeller Plaza, New York 20, N. Y. 6 x 9 in. 174 pp.—Recognizing that adequate plans must be made for the postwar research which must lead industry towards new goals, the Standard Oil Development Co., the central research organization of Standard Oil Co. (New Jersey), made

its Silver Anniversary in October, 1944, the occasion for a Forum on the Future of Industrial Research. The Forum consisted of papers and discussions, all of which are reproduced in this book. Among those contributing papers were Frank B. Jewett, Thomas Midgley, Jr., Harry L. Derby, Bradley Dewey, Edwin H. Land, Westbrook Steele, Earl P. Stevenson, Clyde E. Williams, A. C. Fieldner, and Robert P. Patterson. Participating in the discussion were such outstanding technologists as C. F. Kettering, Lyman J. Briggs, Morehead Patterson, Lammot du Pont, R. W. Gallagher and Frank A. Howard. The latter also contributes an introduction and summary to the book. [From *The Rubber Age* of New York.]

1945 Plastics Catalog. Published by Plastics Catalogue Corp., 122 East 42nd St., New York 17, N. Y. 8½ x 11½ in. 1200 pp. $6.00.—This ninth revised and expanded "encyclopedia of plastics" continues the chronicle of wartime advances achieved by the overall plastics industry, but an innovation is made in the introductory section by the inclusion of a full-color review of the civilian plastics of the past, together with their counterparts of the future as rendered by a group of well-known industrial designers. Another innovation in the latest edition is the inclusion of industry statistical information, covering moulding powder production, compression presses, injection machines, extrusion machines, etc. The first overall price list of plastics is also included, as is a section detailing A.S.T.M. standards. All of the technical material has been completely revised and brought up-to-date, including the section devoted to Synthetic Rubbers and Rubberlike Plastics. Tabular information, in chart form, is furnished on plastics properties, plastics identification, chemical formulas, plastics materials manufacture, solvents, plasticizers, plastics used in liquid coatings, and synthetic rubbers. The Directory Section of the volume contains 10 complete directories to all branches of the plastics industry, including educational institutions, molders, material manufacturers, and trade names. [From *The Rubber Age* of New York.]

Technical Data on Plastics. (Revised). Issued by the Plastics Materials Manufacturers' Association, Tower Building, 14th and K Sts., Washington 5, D. C. 8½ x 11 in. 164 pp. $1.50.—This revised edition, the first since August, 1943, covers 20 types of plastic materials, and tabulates all known data for use of those in industry and government concerned with the application of such materials in the war effort. Material for which data are given are: casein plastic, cast allyl plastics, cast phenolic resins, cellulose acetates, cellulose acetate butyrates, cellulose nitrate, ethylcellulose, laminated phenolic products, melamine moulding materials, methyl methacrylates, Nylon, phenol-formaldehyde moulding materials, phenol-furfural moulding materials, polyethylene plastics, polystyrenes, polyvinyl formals, acetals and butyrals, polyvinyl chloride plastics, urea-formaldehyde moulding materials, vinylidene chloride, and vinyl chloride-acetate resin compounds. Tabulations for each material are divided into two sections, one listing properties bearing primarily on fabrication, the other with strength of the finished product. Effects of temperature and humidity on test values are indicated by graphs in some instances. [From *The Rubber Age* of New York.]

The New Plastics. By H. R. Simonds and M. H. Bigelow. Published by D. Van Nostrand Co., Inc., 250 Fourth Ave., New York 3, N. Y. 6 x 9 in. 316 pp. $4.50.—Issued as a supplement to earlier books on plastics rather

than as a treatise on the subject as a whole, this book brings together for the first time information on all the important plastics materials developed since 1940 and, in addition, presents a round-up of important developments throughout the plastics industry. It covers the composition, methods of manufacture and fabrication, properties, and uses of dozens of new materials, some of which have reached the tonnage stage while others are still in the experimental phase. Data are included on Nylon, the melamine resins, Zinlac, the silicones, Penacolite, Fosterite, new alkyd resins, etc. There are complete chapters on new fibers, organic coatings and adhesives, and laminating materials. A chapter on new processes covers moulding with electronic heating. A special chapter is devoted to synthetic rubbers, with pertinent data on Buna-S, Perbunan, Hycar-OR, Chemigum, Vistanex, Butyl, Thiokol, Paracon, Paraplex X-100, and Marbon-S and S-1. The book has 12 chapters, an appendix giving formulas for most newer plastics, and a complete subject index. [From *The Rubber Age* of New York.]

PLASTICS—SCIENTIFIC AND TECHNOLOGICAL. By H. Ronald Fleck. Published by the Chemical Publishing Co., Inc., 26 Court St., Brooklyn 2, N. Y. 5½ x 8½ in. 326 pp. $6.50.—Originally published in England, and now available in an American edition with some revisions, this book is an up-to-date and comprehensive text on the scientific and technological aspects of the expanding plastics industry. Embracing both the European and American developments, it comprises a critical survey of the literature and a correlation of scattered data which should prove of value to both the technologists of the field and to practical men whose work requires some knowledge of the chemistry and technology of plastics.

The book has 15 chapters in all, as follows: (1) *History of Plastics;* (2) *Raw Materials;* (3) *Theoretical Principles of Polymerization;* (4) *Chemistry of Plastic Materials;* (5) *Manufacture of Plastic Materials;* (6) *Synthetic Elastomers or Rubberlike Plastics;* (7) *Physical Properties of Thermoplastic Materials;* (8) *Physical Properties of Thermosetting Materials;* (9) *Synthetic Resins;* (10) *Synthetic Fibres and Textiles;* (11) *Adhesives, Plywood and Impregnated Wood;* (12) *Manufacture of Dies and Molds;* (13) *Manufacture of Plastic Articles;* (14) *Chemical, Physical and Electrical Testing of Plastics;* (15) *Chemical Analysis of Raw Materials.* In addition, some valuable addenda are furnished and a subject index included.

The chapter on Synthetic Elastomers or Rubberlike Plastics is well handled. It includes reference to the chemistry of natural rubber, a classification of polymers with rubberlike properties, a discussion of raw materials (coal, petroleum, acrylonitrile, ethylene dichloride, isoprene, styrene, vinylacetylene, etc.), a description of the vulcanization theory, flexibility of elastomers at low temperatures, and, finally, an outline of the specific properties of the various copolymers.

Referring to the postwar status of rubber, the author states that "it is fairly evident that since a large mass of people in the Far East depend on rubber for their livelihood, and since natural rubber possesses certain advantages over the synthetic substitutes, rubber will regain a position in the new postwar economy of the world". On the other hand, however, he refers to the fact that the vast new (synthetic rubber) industry cannot be allowed to die out, and adds "it is probable that some equitable distribution between natural rubber and the new elastomers will be achieved". [From *The Rubber Age* of New York.]

THE CHEMICAL FORMULARY. (VOL. VII). Edited by H. Bennett. Published by the Chemical Publishing Co., Inc., 26 Court St., Brooklyn 2, N. Y. 5½ x 8½ in. 474 pp. $6.00.—More than 2,000 formulas for mixing and making thousands of products are included in this latest edition. While all previous volumes of the book, issued biennially for the last twelve years, were designed primarily for experienced chemists and technicians, the latest number has been edited especially for laymen. Each of the seven volumes published to date contains different material, and can be used separately or as a set. Like previous editions, Vol. VII includes formulas for a multiplicity of items, ranging from adhesives to various zinc solutions for rust prevention. It covers the latest scientific discoveries in chemistry and industry, such as DDT insecticides and the newest developments in plastics. The volume also contains an index giving the name and address of mail order firms handling specific products needed for formulary work. [From *The Rubber Age* of New York.]

1945 CLASSIFIED DIRECTORY OF THE ASSOCIATION OF CONSULTING CHEMISTS AND CHEMICAL ENGINEERS, INC. Published by the Association, 50 East 41st St., New York 17, N. Y. 7¾ x 10¾ in. 108 pp.—The latest edition of this directory, the ninth to be published, has been completely revised and brought up-to-date. It comprises three sections, the first listing about one hundred fields of chemistry and engineering, the second describing the qualifications of member consultants and their particular scope of activities, and the third devoted to indexes, including a complete membership list and geographical locations of members. A guide for using the directory most efficiently is also included. [From *The Rubber Age* of New York.]

RECENT ADVANCES IN THE PHYSICS AND CHEMISTRY OF RUBBER *

I. THE SIZE AND SHAPE OF THE RUBBER MOLECULE

GEOFFREY GEE

During the last decade, enormous strides have been made in the scientific study of rubber and related polymers. The main factors combining to make this possible have been the realization that the physical behavior of these materials depends on their long chain character, while their chemical properties are essentially those of a low molecular substance of similar structure. Contrary to earlier belief, neither the physics nor the chemistry of rubber involves any mysterious new forces or reactivities unknown among smaller molecules.

Since such importance attaches to the size and shape of the rubber molecule, we begin by reviewing briefly the evidence on which our present theories are based. Methods of determining molecular weights may be divided into "counting" methods and "weighing" methods. The former include the determination of any of the "colligative" properties of a solution; the latter depends on the use of an ultracentrifuge.

The colligative properties comprise the effects of a solute in lowering the vapor pressure and freezing point of the solvent, in raising its boiling point, and in producing an osmotic pressure. All of these are thermodynamically related, so that measurement of any one permits the remainder to be calculated, at least approximately. The only two which have played any important part in enabling the molecular weight of rubber to be estimated are the freezing point depression, and the osmotic pressure. It is easy to see in a qualitative way how these two properties of a solution are related to the presence and concentration of the solute.

When a liquid freezes, the molecules lose their freedom to wander through the whole bulk under the influence of their thermal energy and settle down into a highly ordered crystalline lattice. If solute molecules are present, the thermal energy of the liquid is but little affected by them, but they hinder the solvent molecules from packing into a crystal lattice, and it is necessary to reduce the thermal energy of the system, *i.e.*, lower the temperature, before crystallization can occur. The extent to which the temperature must be lowered depends on the number of solute molecules present, and can therefore be used to "count" them, and hence to estimate their size. If θ is the freezing point depression produced by c grams of solute molecular weight M_r dissolved in 1 liter of solvent of molecular weight M_o, density C_o, freezing point T_o and

* Reprinted from the *India-Rubber Journal*, Vol. 108, No. 11, pages 289–290, 292–293, March 17, 1945; No. 12, pages 319–320, 322, March 24, 1945; No. 13, pages 349–350, 352, 359–361, March 31, 1945; No. 14, pages 375–376, 378–379, April 7, 1945. These papers represent a series of lectures at Newton Heath Technical School, Manchester, by Geoffrey Gee and L. R. G. Treloar of the British Rubber Producers' Research Association, 48 Tewin Road, Welwyn Garden City, Herts, England.

molar latent heat of fusion L_o, it can be shown that, if the solution is ideal:

$$M_r \simeq \frac{RT_o^2 M_o}{1000 C_o L_o} \frac{c}{\theta} \tag{1}$$

If a solution is separated from its pure solvent by a membrane permeable to the solvent but not to the solute, the former tends to diffuse into the solution. The reason for this is that the membrane is bombarded equally on both sides by molecules, a certain fraction of the impacts of solvent molecules leading to penetration of the membrane. Since only a part of the collisions on the solution side are made by solvent molecules, the number of successful collisions will be less on this side, and there will be a net transference of solvent molecules into the solution. If now a hydrostatic pressure is applied to the solution, but not to the solvent, the number of successful collisions on the solution side of the membrane will be increased, and it is evidently possible to find a pressure such that there will be no net transference of solvent through the membrane. This pressure is, by definition, the osmotic pressure II of the solution, and is also related to the number of solute molecules. It may be shown that, for ideal solutions:

$$\simeq \frac{RT}{M_r} \cdot c \tag{2}$$

When these two methods are applied to rubber solutions, they give results which are, at first sight, very perplexing. The size of the molecule appears to depend on the concentration of the solution and on the nature of the solvent. This phenomenon is quite different, both in nature and magnitude, from the familiar association of solute molecules, *e.g.*, of benzoic acid in benzene. When the solute is associated, its molecular weight increases with concentration to a small multiple of its true value. Rubber solutions, on the other hand, give apparent molecular weights which decrease enormously as the concentration is raised, from about 300,000 in dilute solution to about 3,000 in a 15 per cent solution. The detailed evidence has been summarized in an earlier paper[1], and will not be repeated here. Two alternative conclusions may be drawn from the results: either the rubber "molecule" varies greatly in size according to circumstances, and particularly with concentration, or the equations employed ((1) and (2)) are inapplicable to rubber solutions. Two observations make the first alternative unlikely: (1) that the "molecular weight" decreases with rise of concentration, whereas any process of aggregation would be expected to go in the opposite way, and (2) that the molecular weights obtained from osmotic pressure measurements in a series of solvents differ at any finite concentration, but all tend to the same limiting value of about 300,000 at infinite dilution. It is a natural and legitimate guess that this limiting value is the true molecular weight, and that deviations at finite concentrations are due to errors in the equations. Since these have only been derived for "ideal" solutions, we may say alternatively that rubber solutions do not behave ideally.

Before seeking an explanation of this supposed non-ideality, we must consider the results of molecular weight determinations which involve "weighing" the molecules. In a dilute rubber solution kept at constant temperature, the rubber molecules remain evenly distributed throughout the solution because their thermal energy produces constant diffusion and movement which completely obscure their tendency to sediment or cream (according to the relative densities of rubber and solvent) under the influence of gravity. By putting such a solution in an ultracentrifuge, rotating at a speed of about 1000 revo-

lutions per second, the effective weight of the molecules is increased nearly a million times, and thermal energy is no longer sufficient to prevent the rubber molecules from sedimenting. If the gravitational field is known, measurement of the rate of sedimentation enables one to calculate the weight of the molecules. This method was worked out by Svedborg[2] and applied in the main to proteins in aqueous solutions. Measurements on rubber have been reported by Lansing and Kraemer[3], who find values of the same order of magnitude as those obtained by the osmotic method. This approximate agreement affords strong evidence that the suggested interpretation of the osmotic data is in fact correct.

Why then do rubber solutions fail to obey the usual laws of ideal solutions? The explanation is simply that the derivation of these laws involves the assumption that the molecules of solvent and solute are at least approximately equal in size: it is therefore in no way surprising that they should be inapplicable to rubber solutions. Consideration of the problem of devising modified laws for rubber solutions shows that, in general, the osmotic pressure of a rubber solution of given concentration depends on the shape of the molecule as well as on its size. It has, however, been shown that, for molecules of any size and shape, the laws must reduce at infinite dilution, to those of an ideal solution[4]. Thus, while Equation (2) as it stands is incorrect, we may always write:

$$M_r = RT \operatorname*{Lim}_{c \to 0} \left(\frac{c}{\Pi} \right) \tag{3}$$

This is the form in which we have actually used the equation in deriving molecular weights from osmotic data, and the method is now seen to be theoretically sound.

Two lines of evidence as to the shape of the rubber molecule will be mentioned here; others will occur in the course of the later papers of this series, in the agreement between experiments and the predictions of theories based on a molecular model. We consider first the viscosity of rubber solutions; even at quite low concentrations total rubbers give highly viscous solutions. Now the classical theory of solution viscosity, worked out by Einstein, requires the viscosity of a dilute solution to be very nearly equal to that of the pure solvent. If η, η_0, are the viscosities of solution and solvent, the specific viscosity η_{sp}, defined as $\frac{\eta}{\eta_0} - 1$ is given by Einstein's equation as:

$$\eta_{sp} = 2.5\, v_r \tag{4}$$

where v_r is the volume fraction of solute (cc. per cc. of solution) in the solution. The very large discrepancy between this equation and the behavior of rubber solutions shows that the model used in deriving Equation (4) must have been seriously in error. In fact, Einstein assumed that the solute molecules were small compact spheres, whereas we have to conclude from the experimental results that rubber molecules are not small compact spheres. This same method of investigation enables proteins to be classified rather sharply into globular proteins, which, although of high molecular weight, give mobile solutions, and fibrous proteins, which give solutions of viscosities comparable with those of rubber solutions.

The second line of evidence is based on the chemical nature of natural rubber, which is a polyisoprene:

$$(CH_2—C(CH_3)=CH—CH_2)_n$$

This formulation of rubber shows the molecule as a very long straight chain ($n \sim 5{,}000$), but it has to be borne in mind that three-fourths of the links in the chain are single bonds, around which more or less free rotation is possible. Two conclusions follow from this consideration: (1) that although the rubber molecule is chemically a long chain, it is not to be considered physically as a long stiff fibre; (2) that the molecule has really no static shape; since its thermal energy leads to rotations and relative displacements of parts of the chain, giving the molecule an ever-changing configuration. This point will be taken up more fully in Part II, in which it will be shown that it is possible to calculate a statistically most probable distance between the ends of a molecule, and thus

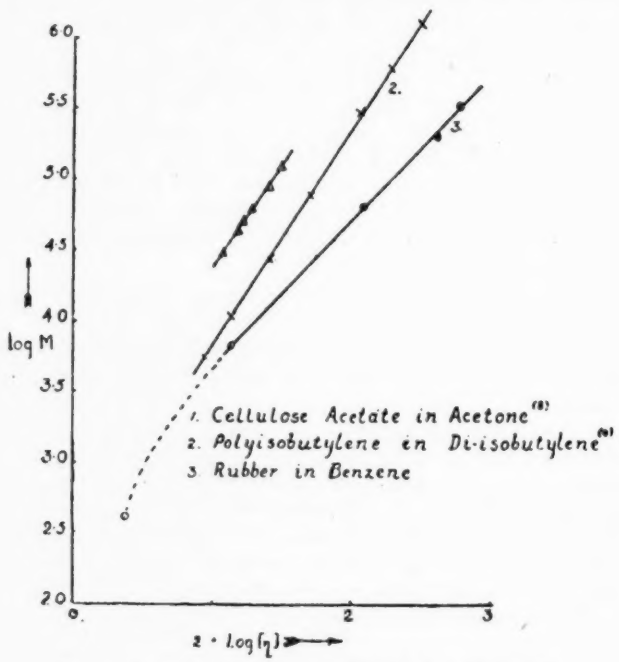

FIG. 1.—Dependence of intrinsic viscosity on molecular weight.

to arrive at the conclusion that the molecule is, on the average, highly kinked into a very loose and open, more or less spherical, tangle. In solid rubber different molecules must interpenetrate one another extensively, but in a sufficiently dilute solution, the space within the "envelope" formed by the outermost parts of a single molecule is filled with solvent molecules. For rubber of molecular weight 300,000, a rough calculation shows that the molecules are independent of one another only in very dilute solutions of concentration $\gg 0.1$ per cent. The very high viscosity of a 1 per cent rubber solution therefore finds a natural explanation in the mutual interference of the molecules with one another, producing a transient structure which has to be broken down when the solution is sheared.

The high viscosity of very dilute rubber solutions arises in a different way. When the solution is sheared, different parts of a single rubber molecule lie in layers which are being displaced relative to one another. There is a tendency

for the molecule to be stretched in the direction of flow, and there is also relative motion of the liquid past it. Both these factors add to the normal frictional resistance encountered in the pure liquid, and thus impart a high viscosity to the solution. Quantitative treatments[5] of this problem suggest that the "intrinsic viscosity" $[\eta]$ of a solution, defined as the limiting value at infinite dilution of the quotient η_{sp}/c, should be proportional to the molecular weight of the polymer, or some small power of it, *i.e.*:

$$[\eta] = kM^{\beta} \tag{5}$$

or

$$\log [\eta] = \log k + \beta \log M \tag{5'}$$

Thus a plot of $\log [\eta]$ against $\log M$ should be linear, and Figure 1 shows this to hold very well for natural rubber and for other polymers. It is to be noted that, in general, β is not exactly unity, but rather less, while both β and k may depend on the nature of the solvent. Equation (5) is a generalization of the familiar empirical equation of Staudinger, in which β was assumed to be 1. It clearly offers another alternative method of obtaining molecular weights, but its usefulness in this direction is limited by two factors: (1) that k and β have to be determined by reference to an absolute method (*e.g.*, osmotic) and (2) if the rubber is not homogeneous, the value of M obtained from Equation (5) is, in general, higher than that found osmotically. This discrepancy, which arises from the fact that the two methods give different kinds of "average" molecular weight, would probably not usually exceed a factor of two, and does not prevent the use of viscosity data to give valuable information as to the relative molecular weights of different samples of the same rubber[6].

Finally, we return to the problem of the departure of rubber solutions from the laws of ideal solutions. We have already noted that this is inherent in the large size of the rubber molecule. In the last few years it has proved possible to calculate the colligative properties of rubber solutions, assuming the molecule to have the size and shape indicated by the evidence outlined above. It is beyond the scope of this paper to try and outline this theory, but it should be recorded that a semiquantitative understanding of polymer solutions has been achieved in this way[7]. The physical significance of the conclusions may be put very crudely by saying that the rubber molecule in solution is the effective unit in determining properties only at very high dilution. As the concentration is increased, the molecule behaves as though it were built up of an increasing number of semi-independent segments. We can indeed see that this conclusion is inherent in the picture we have built up of the size and shape of the rubber molecule.

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II. THE KINETIC THEORY OF RUBBER ELASTICITY

L. R. G. Treloar

In Part I, the nature of the rubber molecule was discussed, and it was shown to consist essentially of a single chain of relatively very great length. Many of the characteristics of rubber, such as the high viscosity of rubber solutions, the high elasticity, and the capacity for swelling in solvents, are directly connected with this fundamental molecular structure. The present Part II is concerned with the elasticity of rubber, and discusses the origin of the remarkable difference between the elastic properties of rubber and ordinary hard solids. The typical solid, *e.g.*, a rock salt crystal, is represented by a structure in which each atom is held in an equilibrium position by strong forces. The application of a deforming force disturbs the equilibrium positions of the atoms very slightly, in such a way that internal stresses which balance the externally applied force are brought into play. The value of Young's modulus for a crystal is of the order 10^{11}, and the maximum extension before breakage occurs is generally about 1 per cent. Rubbers on the other hand can be deformed by 700 per cent or more by comparatively small forces, corresponding to Young's moduli of the order 10^7. These enormous differences point to a different elastic mechanism in the two cases.

When we look at the range of materials which show rubberlike elasticity, we find in all cases the same fundamental pattern of molecular structure. The atomic constituents of the molecule may vary, but the molecule invariably takes the form of a very long chain, generally, but not necessarily of carbon atoms. It is this basic similarity which provides the clue to the understanding of the phenomenon of high elasticity.

THE ORIGIN OF THE ELASTICITY

Until about twelve years ago, none of the theories of the elasticity of rubber which had been proposed could be regarded as even approximately satisfactory. Attempts to interpret long-range elasticity on the basis of interatomic forces were manifestly inadequate, and it was not until Meyer, von Susich and Valko[1] introduced the concept of a dynamic, in contrast to a static, basis for the phenomenon, that the mystery was solved. The theory developed rapidly through the work of Guth and Mark[2] and of Kuhn[3], and is now generally accepted as representing the correct method of approach.

To understand the kinetic viewpoint, we must first examine the form of a long-chain molecule, considered as an isolated unit. For this purpose it is usual to consider the simplest possible chain structure, namely, the paraffin molecule. The assumption is made that the carbon atoms of the chain are in a state of continual thermal vibration, so that they may take up any relative positions consistent with the maintenance of a fixed bond length and a fixed angle between bonds ($109\frac{1}{2}°$). According to this assumption, each C-C bond may be regarded as rotating freely about the preceding bond as axis. There is chemical evidence that such rotation does take place. In consequence of this random rotation about bonds, the chain is not a uniform zigzag in one plane, as in Figure 1(a), but assumes a randomly-kinked form in 3-dimensions, as indicated in Figure 1(b). The distance between the ends of the chain in this form is likely to be very much less than the outstretched length of the molecule in Figure 1(a), and the statistical treatment of the problem enables

the probability of any given end-to-end distance to be calculated. The function representing this probability turns out to be the ordinary Gaussian error function, which is represented in Figure 2. The normal state of the free molecule may be identified with the maximum of this curve, *i.e.*, it is the most probable state, and the corresponding length is found to be proportional to the square root of the number of "links" in the chain.

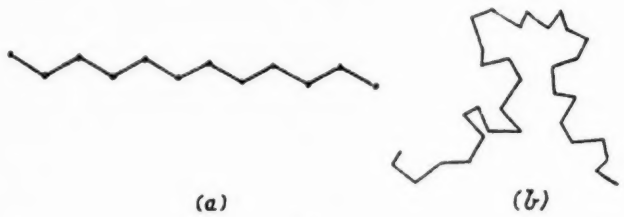

FIG. 1

We see then, that if the molecule is forcibly extended and then released, the random thermal motion rapidly restores it to a length not very different from the statistically most probable length. The molecule therefore exhibits elasticity. Moreover, its elastic extensibility is proportional to the square root of the number of chain links, or the molecular weight. This theory, therefore, explains in a natural manner why long-range extensibility is found only in association with chainlike molecules of very great length.

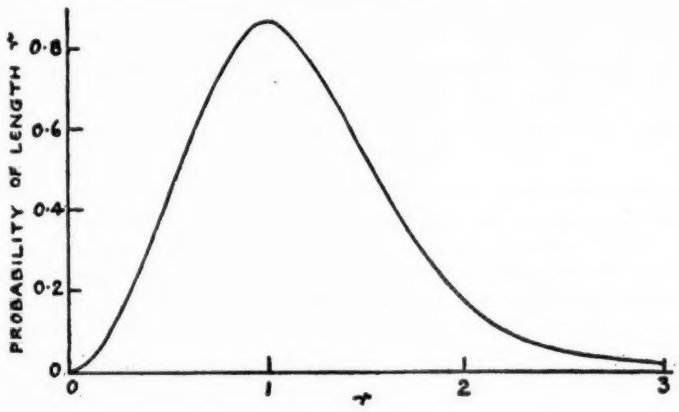

FIG. 2

The thermodynamic development of the kinetic theory leads to some rather striking conclusions. Two of the more important of these are:

(a) In rubber held at constant extension, the tension is proportional to the absolute temperature.

(b) The extension of rubber takes place without change in its internal energy; hence there is an evolution of heat equal to the work done on the rubber by the stretching force.

The first of these effects was tested experimentally by Meyer and Ferri[4] in 1935, who showed that, for a vulcanized rubber containing 8 per cent of sulfur,

the theoretical relationship was accurately obeyed over a range of more than 100° C within certain limits of extension. The second effect is well known, but a quantitative agreement between the work of extension and the heat evolved has not been obtained, chiefly because of the complicating effects, with which is associated a latent heat. However, these two effects are so entirely different from what is found in ordinary solids under similar conditions that the degree of agreement between theory and experiment may be considered highly satisfactory.

THE IDEAL RUBBER

This far our attention has been focused on the individual molecule. We have yet to consider in more detail how the elastic properties of the molecule are to be conveyed to the material in bulk. When we consider this problem we see that, in order to be able to take up a variety of statistical forms in the way required by the theory, the molecular chains must have a freedom of movement comparable with that in a liquid. On the other hand, for the rubber to maintain a permanent shape, and to resist applied stresses, the molecules must somehow be fixed in their average positions relative to one another. To meet these two rather contradictory requirements it is necessary to think of the molecules as linked together by a relatively small number of unbreakable bonds. These are present in sufficient numbers to produce a complete three-dimensional network throughout the material but, owing to the great length of the chains, they need not seriously impede the freedom of motion of the segments of molecules between such points of junction.

We are thus led to postulate three necessary conditions for the occurrence of rubberlike elasticity:

(1) the presence of long-chain molecules, with freely-rotating links;
(2) weak secondary forces around these molecules;
(3) a few points of cross-linkage, resulting in a loose three-dimensional network.

The ideal rubber may be thought of as a permanent network of long-chain molecules held together by unbreakable bonds, but otherwise completely free to move. The stress-strain properties of such an ideal network have been worked out by a number of authors. The most satisfactory development in this direction is due to Wall[5], who obtained the following equations for the case of a simple elongation (or unidirectional compression) and simple shear, respectively:

For elongation $F_\alpha = NkT\left(\alpha - \frac{1}{\alpha}\right)$

(F_α = stretching force, referred to original section of 1 sq. cm., N = no. of "molecules", a "molecule" being the length of chain between its points of junction to the network, k = Boltzmann's constant, T = absolute temperature, and α = ratio of stretched to unstretched length.)

For simple shear $F\sigma = NkT\sigma$

($F\sigma$ = shear stress, σ = amount of shear.)

There are a number of particularly interesting features of these equations. Firstly, the stress-strain curve for elongation is nonlinear, *i.e.*, Hooke's Law

does not apply, while for shear the relation is linear. Secondly, the only molecular property which enters into these equations is N, the number of chain elements in the network. This quantity is simply related to the "molecular weight" of the chain. The precise constitution of the molecule, or the number of freely rotating links which it contains, is of no significance in this connection. The third point, which is related to this, is that only one physical constant is sufficient to define the elastic properties of a highly elastic material.

I have extended the elastic network theory to the case of a deformation of any type, and have shown experimentally that the resultant equations give a reasonably satisfactory account of the properties of well vulcanized rubber under a number of different types of deformation, except under very high strains, when the underlying assumptions of the theory are no longer applicable.

APPLICATION TO REAL MATERIALS

Having now defined the conditions under which rubberlike behavior is to be expected, let us look at some real materials, and enquire to what extent they satisfy these conditions, and the way in which their nonfulfilment leads to departures from the simple behavior of the ideal rubber.

The first point of difference is that in practice rubberlike properties appear only within a certain range of temperature. At low temperatures rubbers transform to a glass-hard condition. Below the transition temperature the molecular chains become immobile, for the thermal energy is no longer sufficient to overcome the secondary forces between the molecules. For a material like natural rubber these secondary forces are relatively weak, and the transition temperature is very low (−70° C). If the intermolecular forces are comparatively strong, the transition temperature is very much higher. This is exemplified by polymethylmethacrylate, which is a glass at normal temperatures (extensively used for its nonsplintering property), but becomes highly elastic above about 70° C.

Rubberlike properties may also be lost at high temperatures, where, in the case of polymers which are not cross-linked, the molecules become sufficiently mobile to slide bodily past one another, the rubber thus becoming a viscous liquid. The longer the molecules, the higher the temperature at which this effect becomes noticeable. This plastic flow occurs in raw rubber, in which there are no true cross-links between molecules, but only what may be called entanglement cohesions, *i.e.*, complex mechanical entanglements held together with varying degrees of permanence by the secondary forces.

The rubberlike state is thus limited at low temperatures by the magnitude of the secondary forces tending to produce complete rigidity, and at high temperatures by the strength of the intermolecular cross-links responsible for the maintenance of the structure. We shall also have to consider another factor which may interfere with rubberlike behavior, namely crystallization. This will be the subject of a later paper.

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III. THE SOLUBILITY AND SWELLING OF RUBBERS

GEOFFREY GEE

In Parts I and II we have built up a picture of the molecular structure of a piece of rubber, which we have envisaged as a mass of interpenetrating chains, each of considerable length, but randomly kinked and in constant thermal motion, so that its shape is continually changing. Vulcanization restricts the possible motions of the mass by introducing permanent connections between pairs of chains at a series of irregularly spaced points. The purpose of Part III is to show how the picture can be extended to account for the behavior of such a system in contact with a liquid.

If we imagine a liquid as a mass of more or less spherical molecules in constant thermal motion, it is clear that, when a liquid is brought into contact with a rubber, there is a tendency for molecules of liquid to diffuse into the rubber structure. Considering first the case of an unvulcanized rubber, we should expect the liquid to enter in increasing amounts, thereby separating the rubber chains and giving them very much greater freedom of motion, until finally some of them begin to find their way out of the main body of rubber and into the liquid. The rubber would thus be observed first to swell and then slowly to disperse until a uniform mixture of rubber and liquid is produced. This is, of course, the behavior actually observed when raw rubber is brought into contact with a liquid in which it is soluble. It is important to emphasize that the driving force which causes the mixing is simply the thermal motion of the components, and is not essentially dependent on any molecular attraction between rubber and liquid. It can be given a quantitative measure in terms of the thermodynamic concept of the increase of entropy consequent on mixing, but this development will not be considered here, our purpose being only to discuss the essential physical basis of the phenomenon[1].

In well vulcanized rubber, no chains are free to diffuse out into the liquid, and the liquid can diffuse into the rubber only by extending the network. Since this distension causes the chains of the network to take up configurations of smaller probability, the network exerts an elastic reaction which tends to squeeze out the liquid. A point is ultimately reached at which the elastic reaction of the network just balances the thermal tendency of the liquid to diffuse in, and swelling then reaches a definite limit, depending on the closeness of the network structure.

The above account of the solution and swelling of rubber suggests that any raw rubber should be soluble in any liquid, and that all liquids should be equally good swelling agents for a given vulcanizate. This is so very far from the truth that it is obvious that an important factor must have been neglected and, in fact, we have to take account of intermolecular forces, both in the rubber and the liquid. The process of diffusion of a molecule of liquid into the rubber involves three steps resulting in energy changes; in practice they occur together, but we may imagine them as three discrete acts: (1) the separation of a molecule of liquid from its neighbors, (2) the separation of chains of the rubber structure sufficiently to create a hole into which (3) the molecule is inserted. In the first two steps work has to be done against the cohesion of the materials and energy is required equal in step (1) to the latent heat of evaporation of the liquid at constant volume, and in step (2) to a corresponding quantity for the rubber. Introduction of the liquid into the hole is a conden-

sation process, in which energy is recovered, in an amount which nearly balances that previously expended. The balance of energy appears as heat, and since in general the energy absorbed in (1) and (2) exceeds that recovered in (3), heat is absorbed, and the system cools slightly. Now the net energy represented by this heat absorption has to be provided at the expense of the thermal motion which constitutes the driving force in causing mixing. If, then, the heat absorption is large for a particular combination of rubber and liquid, the liquid in question is not a solvent for that rubber. Furthermore, if we have a selected vulcanized rubber, its swelling in a series of liquids decreases as their heats of mixing with the rubber increase.

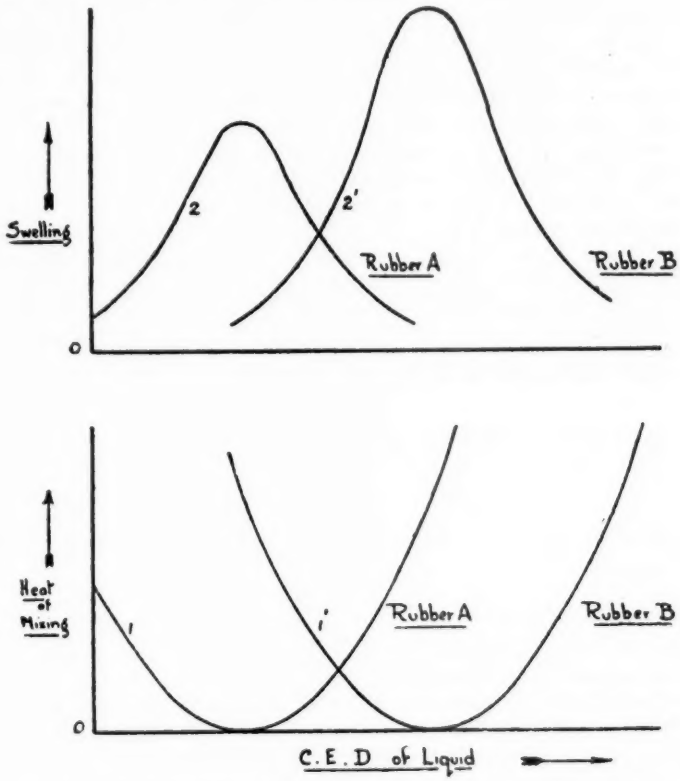

FIG. 1.—Dependence of heat of mixing and swelling on cohesive energy density.

So far, our account has been purely qualitative; before it can be of much practical service it is necessary to consider the factors which determine the magnitude of the heat of mixing. The first obvious one is the size of the liquid molecule; other things being equal, the larger the molecule, the greater is its heat of mixing with rubber and, hence, the smaller its swelling power.

Generally, the most important factor in determining the heat of mixing of a rubber and a liquid is the difference between their cohesive energy densities (C.E.D.). The C.E.D. of a material is the energy required to separate completely all the molecules in 1 cc. of the material, and is equal, for a liquid, to

the latent heat of evaporation per cc. at constant volume. To a first approximation the heat of mixing is proportional[2] to $(\sqrt{e_o} - \sqrt{e_r})^2$ where e_o and e_r are the C.E.D.s of the liquid and rubber, respectively. If now we arrange a series of liquids in order of increasing C.E.D., their heats of mixing with a given rubber pass through a minimum ($\simeq 0$) at $e_o = e_r$, as shown in Figure 1 (curves 1, 1′). The swelling of a vulcanizate of this rubber in the same series of liquids passes through a maximum at this point (curves 2, 2′ of Figure 1). The height of the maximum is determined mainly by the degree of cross-linking of the rubber; the swelling in poor swelling agents is controlled rather by the magnitude of the heat of mixing, and is practically the same for raw rubber as for vulcanizates. Solvents for raw rubber are found among liquids having a small heat of mixing, *i.e.*, $e_o \simeq e_r$. This very general analysis has been shown[2] to account for the general features of the extensive swelling data on natural rubber compiled by Whitby, Evans and Pasternack[3]. If we introduce the effect of the molecular volume V_o of the liquid, it can be shown that the function determining the swelling is $V_o (\sqrt{e_o} - \sqrt{e_r})^2$.

It is clear that a study of the swelling of a given vulcanizate in a selected range of liquids can be used to find e_r, the C.E.D. of the rubber, by making use of the condition for maximum swelling $e_o = e_r$. Given this value, a plot of the swelling Q against $\sqrt{V_o}(\sqrt{e_o} - \sqrt{e_r})$ should be approximately symmetrical, passing through a maximum at $\sqrt{V_o}(\sqrt{e_o} - \sqrt{e_r}) = 0$. A systematic study of the swelling of a number of natural and synthetic rubbers in such a range of liquids has been fully reported elsewhere[4]. The results of five natural rubber vulcanizates are reproduced in Figure 2. These five compounds were of very varied type, their composition being given in Table I.

TABLE I

RUBBER COMPOUNDS USED IN SWELLING MEASUREMENTS

	Parts by weight in compound				
	1	2	3	4	5
Smoked sheet	100	100	100	100	100
Sulfur	3.5	3	3	3	3
Zinc oxide	6	18	100	5	5
Stearic acid	0.5	1.5	2.5	3	3
Mercaptobenzothiazole	0.5	1	—	1	1
Carbon black	—	—	—	45	100
Nonox-S	—	1	1	1.5	1.5
Pine tar	—	3.5	—	1	2
Tetramethylthiuram disulfide	—	—	1	—	0.1
Magnesium carbonate	—	42	50	—	—
Mineral oil	—	—	5	—	—
Magnesium oxide	—	4	—	—	—
Red oxide	—	14	—	—	—
Lithopone	—	64	—	—	—
Paraffin wax	—	1.5	—	—	—
Total	110.5	253.5	262.5	159.5	215.6

All compounds were vulcanized for 30 minutes at 40 lbs. steam pressure.

Several points about these results call for comment:

(1) Detailed experimental points are shown for the pure-gum mix, and it will be noted that, on the whole, they fall very well on the curve, the position of a liquid being almost independent of its chemical nature, as, of course, it should be if this simple theory is correct. For some of the synthetic rubbers

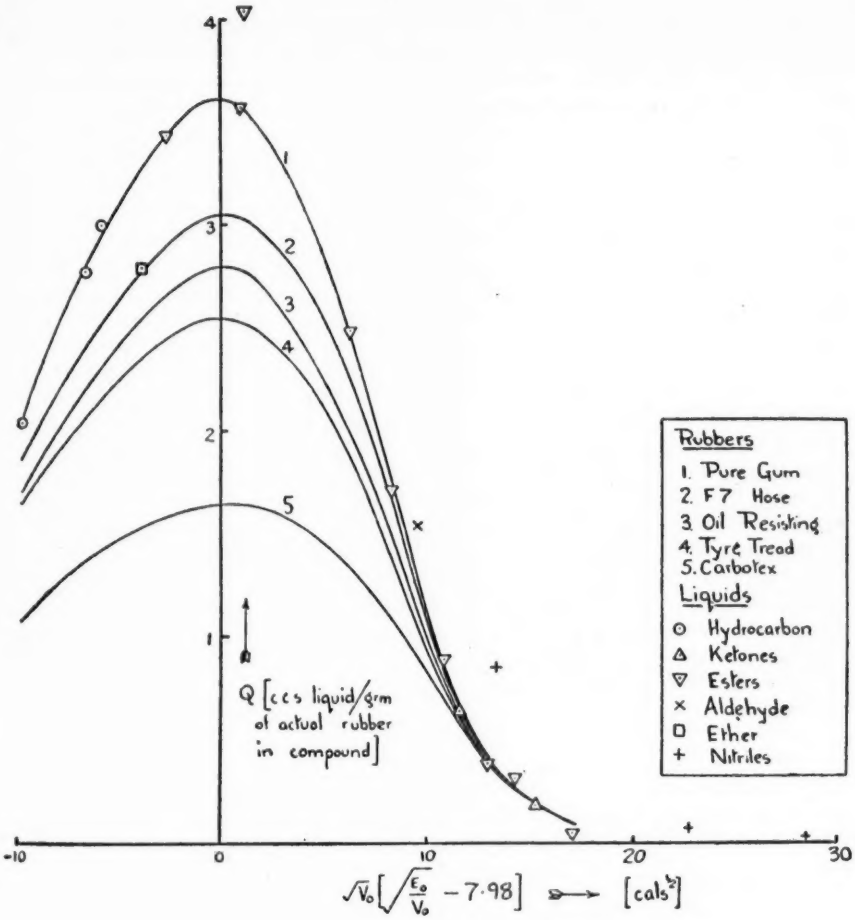

FIG. 2

this does not hold nearly so well. Thus, for Buna-N, ketones and nitriles are somewhat better swelling agents than esters of similar C.E.D., and give points lying on a higher curve than that defined by the esters (Figure 3).

(2) The curves for the five natural rubber compounds are all very similar in shape, and it is clear that the fundamental nature of the swelling is in no way altered by even such wide changes in compounding. The observed swelling of Compounds 2 and 3, both supposedly "oil resisting", is certainly much less than that of the pure-gum compound, but the effect is essentially one of dilution, and is eliminated from Figure 2 by referring swelling to the actual rubber content. Carbon black has a more pronounced effect in reducing swelling, no doubt by strengthening the network; there is no indication of any change in the C.E.D. of the rubber. In agreement with what has been said above, all compounds swell to the same extent in a poor swelling agent.

(3) The value of e_r for natural rubber derived from these measurements is 7.98^2, *i.e.*, 63.7 calories per cc., which is approximately that to be expected from its chemical nature[5].

When we change from natural rubber to one of the synthetics, the only essential difference to be expected, according to our general picture, is in the value of e_r. Since nearly all the synthetics contain polar groups, they are of higher C.E.D. than natural rubber. The maximum of the swelling curve will,

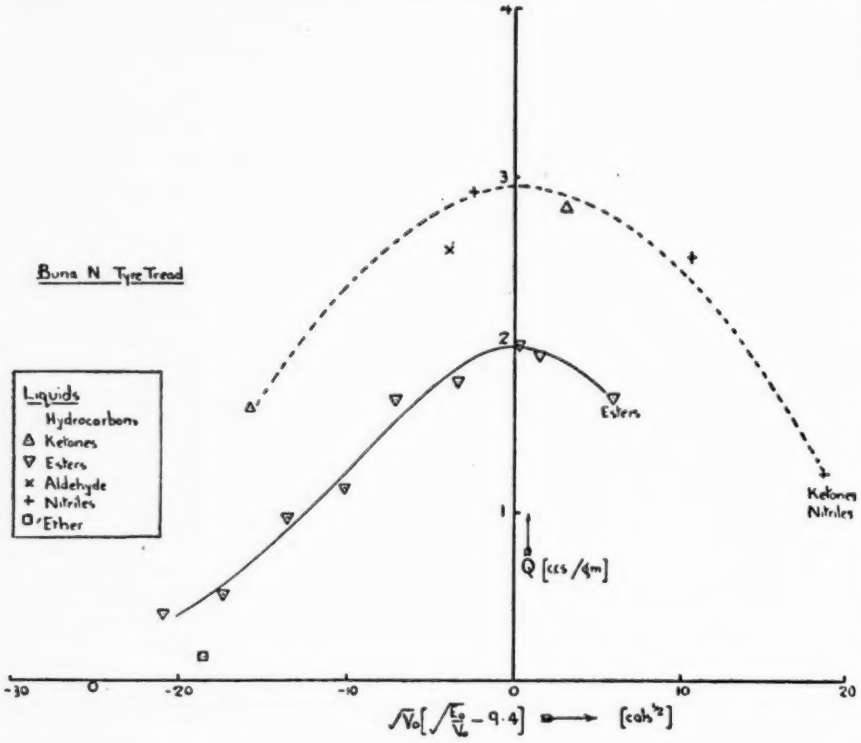

FIG. 3

therefore, be shifted to liquids of higher C.E.D., and this is what is actually found. The C.E.D.s of a series of rubbers, estimated from their swelling behavior, are as follows:

TABLE II

COHESIVE ENERGY DENSITIES OF RUBBERS

Rubber	C.E.D. (calories per cc.)
Natural	63.7
Buna-S	65.5
Neoprene-GN	67
Thiokol-RD	81
Thiokol-F	88
Thiokol-FA	88
Buna-N	88

The effect of this shift of C.E.D. is, of course, to alter the type of liquids to which the rubber is most susceptible. Thus whereas natural rubber swells in naphtha and hydrocarbons generally, but is resistant to acetone, the reverse is

true of Buna-N. In other words, the high C.E.D. of some of the synthetic rubbers is the essential reason for their resistance to naphtha.

It has already been noted that the theory is less satisfactory for synthetic rubbers than for natural rubber, and indeed this is to be expected, since we have treated rubber as a homogeneous material, whereas the high polarity of, *e.g.*, Buna-N, is confined to one of the constituents of the copolymer. The figure assigned to the C.E.D. is therefore only some sort of average, and it is a little surprising that the theory works so well as it does.

It is not difficult to find exceptions in the case of natural rubber[6], and it must be stressed that the theory which has been outlined is only regarded as describing the essential physical basis of swelling; its quantitative accuracy in any particular case must depend on a number of other factors which have to be neglected in any general theory, *e.g.*, association of one or both components, and specific interaction between them.

Mixed Liquids.—The growing use of mixed fuels makes it important to try and understand the effects of admixture on the solvent and swelling power of liquids. It is well known empirically that the properties of mixtures are not necessarily intermediate between those of the components, but no satisfactory theory has been forthcoming until quite recently[7].

If we consider a piece of rubber R immersed in a mixture of two liquids L_1 and L_2, it is clear that thermal motions tend to cause the three components to mix uniformly, and that this tendency is essentially the same as in a binary system. The position regarding intermolecular energies is now very much more complex, since six different types of contact are possible, *viz.*, R—R, L_1—L_1, L_2—L_2, L_1—L_2, R—L_1, R—L_2. The total energy of the system can be expressed in terms of three constants, representing the heats of mixing of the three components taken in pairs. If e_r, e_1 and e_2 are the C.E.D.s the constants will be as follows:

Mixture of L_1 and L_2, Heat of mixing $\alpha \sim (\sqrt{e_1} - \sqrt{e_2})^2$
Mixture of rubber and liquid 1, Heat of mixing $\beta \sim (\sqrt{e_1} - \sqrt{e_r})^2$
Mixture of rubber and liquid 2, Heat of mixing $\gamma \sim (\sqrt{e_2} - \sqrt{e_r})^2$

We have seen that thermal motions tend to drive liquids 1 and 2 into the rubber; this tendency is resisted by intermolecular forces to the extent that the energy of the whole system is thereby increased. The magnitude of this increase clearly depends on α as well as on β and γ, for if α is large, the liquid mixture is already in a state of rather high energy, and transfer of either liquid from the mixture is energetically easier than from the pure liquid. This situation may perhaps be put rather more clearly if we endow the molecules with some anthropomorphic characteristics. We may say that, if α is large, it means that L_1 and L_2 are unhappy in one another's company and may, therefore, prefer to associate with R, even though they might normally have shunned it. Mathematical analysis confirms the conclusion from this general argument, that if two liquids have a large heat of mixing with one another their mixtures have a greater solvent and swelling power than the mean of the components.

The relation between the constants α, β, γ and the C.E.D.s of the components enables us to predict when α is large compared with β and γ; the condition is simply that e_r shall lie between e_1 and e_2, preferably nearly midway. A striking example of this is furnished by the behavior of Neoprene-GN in mixtures of hexane and methyl acetate. The C.E.D.s are: hexane 55, Neo-

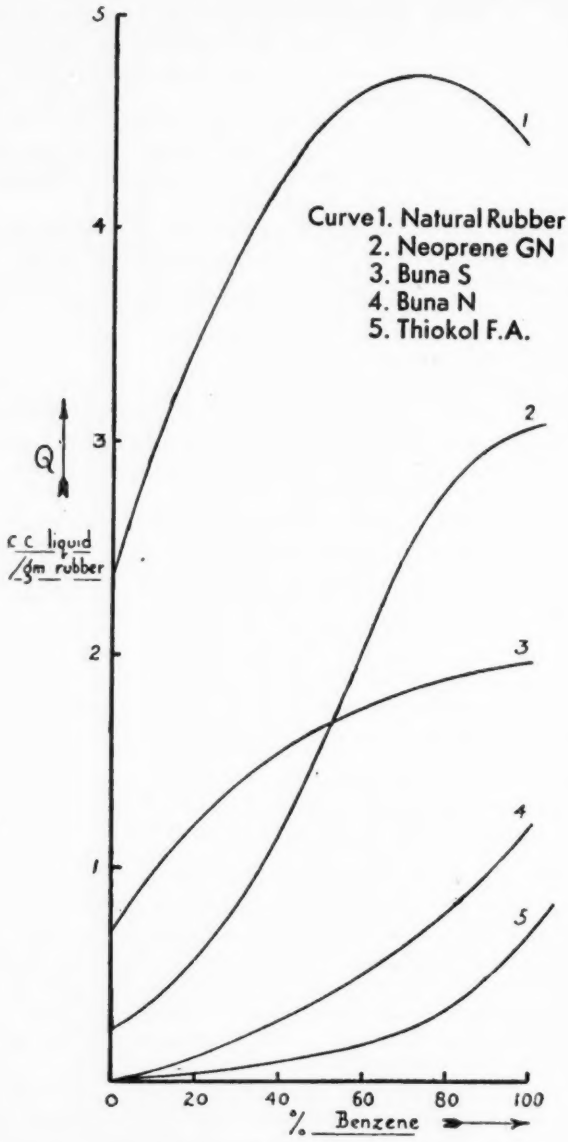

FIG. 4.—Swelling in mixtures of 40/60 petroleum ether + benzene.

prene-GN 67, methyl acetate 92 calories per cc., and neither liquid has much solvent or swelling action on milled Neoprene-GN. The rubber dissolves readily in a 50/50 mixture of the two liquids, and can be precipitated from solution by adding excess of either component.

An interesting and important mixture is that of naphtha with benzene, and Figure 4 shows some swelling data for five vulcanized rubbers in a range of mixtures of 40/60 petroleum ether + benzene. For this pair of liquids, α is

fairly large (calorimetric estimate 9 calories per cc.). For natural rubber β and γ are relatively small, and accordingly mixtures should show enhanced swelling power. This is very evident in Curve 1 of Figure 4, which shows maximum swelling to occur in a mixture containing 70 per cent benzene. For Neoprene-GN and Buna-S, we also have β and γ smaller than α and, although no maximum appears in Curves 2 and 3, it is clear that small additions of naphtha to benzene reduce its swelling power much less than would have been expected. Curves 4 and 5 (Buna-N and Thiokol-FA) are of the form required when interaction between the liquids is negligible: in both these cases β (rubber + petroleum ether) is large compared with α.

Figure 5 shows a number of examples of swelling vulcanized Buna-S in mixed liquids, chosen to cover a range of possible combinations of α, β, γ.

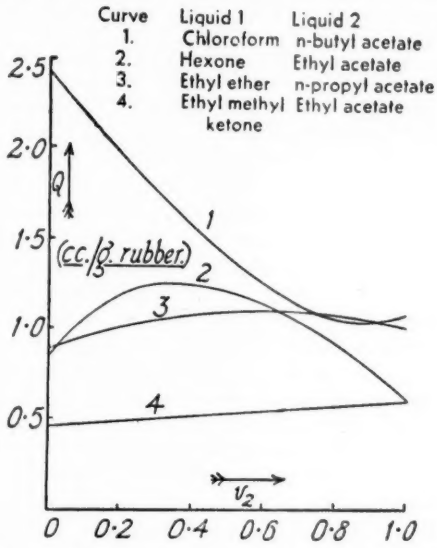

FIG. 5.—Swelling of vulcanized Buna-S in mixed liquids.

Curve 2 is of the type already discussed, in which α is large compared with β and γ. Curves 3 and 4 are examples of $\alpha \simeq 0$, and it will be noted that the swelling is almost independent of the liquid composition. Curve 1 is a rather unusual example of a pair of liquids for which α has a large negative value. Interaction between the liquids should therefore lead to a reduced swelling power, and it is consistent with this prediction that small additions of the very powerful swelling agent $CHCl_3$ are found to reduce slightly the swelling power of the much less active *n*-butyl acetate.

In conclusion, it may be fairly claimed that the ideas advanced above give a satisfactory qualitative and semiquantitative account of the solvent and swelling action of single and mixed liquids.

It appears certain that any real advance towards quantitative accuracy in particular cases must be made at the expense of generality, and must involve increasing complexity. The theories which have been presented are offered as a useful working guide; it is necessary in using them to bear in mind that they are only approximately valid, and to be on the lookout for factors likely to introduce departures from normal behavior.

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[1] For a thermodynamic treatment, see the detailed references below. See also Gee, *Ann. Repts.* **1942**, p. 7.
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IV. CRYSTALLIZATION IN RUBBERS

L. R. G. Treloar

In dealing with elasticity and with swelling, we have thus far considered rubber to be composed of a loose network of randomly-kinked long-chain molecules. This simple picture does not fully represent the structure of rubber under all conditions, and gives no explanation of many of the remarkable physical properties of raw rubber. For a more adequate representation we are forced to include the effects of crystallization. In this Part we shall examine some of these effects, and see what light they throw on the mechanism of the process of crystallization and on the structure of rubber generally.

At the outset we may find some difficulty in accepting the theory that rubber may contain a crystalline phase. This is because we are accustomed to think of a crystal as possessing a precise geometrical shape. We cannot identify such geometrical forms in rubber. But, on consideration, we see that the essential attribute of a crystal is the internal regularity of the spacing of its constituent atoms. The external geometrical regularity, where it exists, is derived from this more fundamental internal structural regularity. It is frequently found, however, that the internal regularity is not accompanied by external regularity. This is true, for example, of the metals, which are invariably crystalline. The absence of external regularity is due to the small size of the individual crystallites. The same considerations apply to rubbers.

Raw rubber may be crystallized either by freezing or by stretching. Frozen crystalline rubber, which is waxy in appearance, is comparatively inelastic, though still flexible. Crystallization in the unstretched state takes about 10 days at 0° C, but is more rapid at lower temperatures, taking only a few hours at −20° C. At still lower temperatures the rate of crystallization is again reduced, and at temperatures below −40° C there is no crystallization at all. In the long time required for crystallization, rubbers stand in marked contrast to liquids (of low molecular weight), which normally crystallize almost instantaneously. In other respects also, there are important differences in the crystallization of rubber and of low-molecular liquids. It is found that the "melting" of crystalline rubber does not occur at a sharply defined temperature, but takes place over a range of about 10° C. For raw rubber crystallized at 0° C, melting starts at about 6° C, and is complete only when the temperature is raised to 16° C[1]. Moreover, the melting temperature depends on the temperature at which crystallization is effected, and is lower the lower the temperature of crystallization. Crystallization in rubber is never complete, and the percentage of crystalline material increases slowly over a period of years. At the same time there is a corresponding increase both in the value and in the definiteness of the melting temperature, pointing to an increasing stability of the crystalline state with the lapse of time.

These effects, namely, the difference between the melting and freezing temperatures, and the dependence of the melting temperature on the conditions under which crystallization occurs, point to the absence of a true equilibrium between the crystalline and amorphous components in the rubber.

The crystallization produced on extension, either in raw or in vulcanized rubber, leads to other effects which are not readily fitted in to our ordinary conceptions of crystallization. In stretched raw rubber, release of the stretching force is not normally accompanied by retraction to the unstretched form; this occurs only when the temperature is raised sufficiently to allow of melting of the crystals formed on extension. The retraction, or melting temperature, is fairly sharp (generally covering not more than 1° C), but its value depends on the temperature of extension, though not on the magnitude of the extension.

On the other hand, there are certain similarities between the crystallization process in rubber and in low-molecular liquids. In both, crystallization is accompanied by the evolution of heat (latent heat), and by a change (usually an increase) in density. Again, just as many crystals are doubly refractive (or birefringent), so are the crystals in rubber. Both the change in density and the birefringence may be employed to give a quantitative measure of the amount of crystalline material present in a given piece of rubber. Studies based on these properties have yielded much information on the phenomena of crystallization in rubber.

THE GROWTH OF CRYSTALLIZATION

Density Method.—To study the crystallization in raw rubber, both unstretched, and under different extensions, strips of smooth sheet suitably clamped were kept at 0° C, and at intervals pieces were cut from the strips for the measurement of density (also carried out at 0° C). The density was

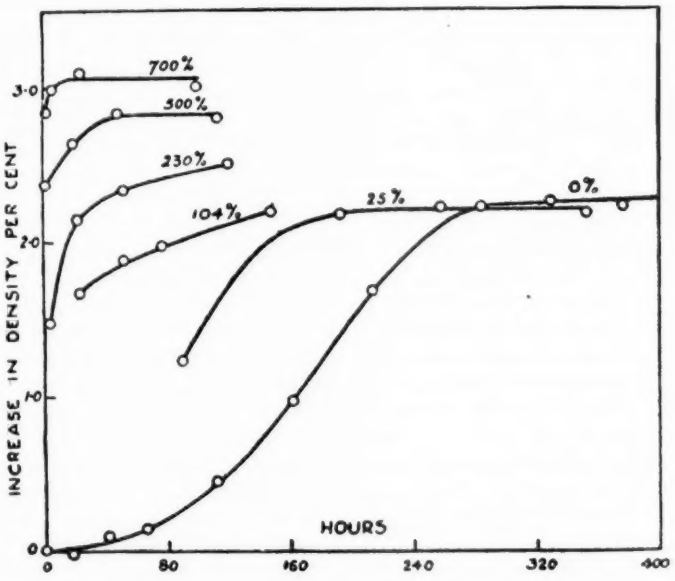

FIG. 1.—Density changes in raw rubber held at the extensions indicated. Temperature 0° C.

deduced from the weights of the specimen in air and in water, respectively. After its density had been obtained, the specimen was warmed, and its density in the amorphous state was determined; thus the density difference due to crystallization was obtained for each specimen.

The results of these experiments are shown in Figure 1[2]. Since the specimens were only removed when crystallization had proceeded to the stage where no retraction of length occurred on removal from the clamps, the earlier stages of crystallization are not shown. There is sufficient information, however, for the conclusion to be drawn that both the rate of crystallization and the final proportion of the crystalline phase increase with the extension.

Birefringence Method.—A very similar picture is presented by the variations in double refraction accompanying crystallization at 0° C, shown in Figure 2[2].

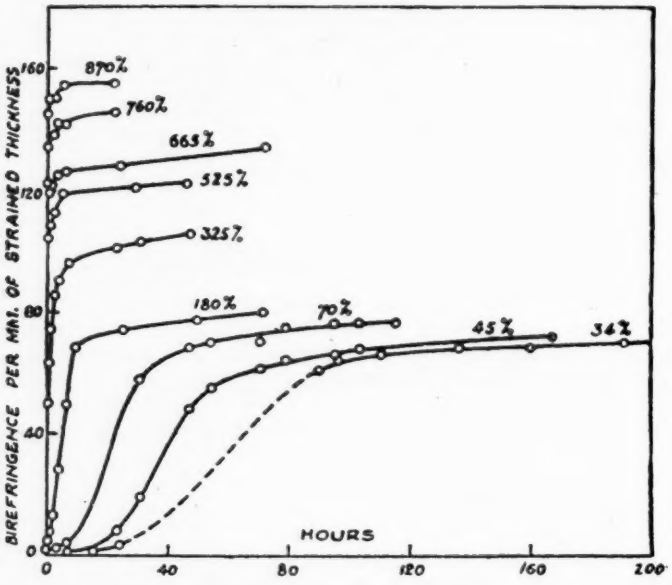

FIG. 2.—Changes in double refraction in raw rubber, held at extension indicated. Temperature 0° C.

An exact comparison shows that, at all but the lowest extensions, the changes in density and the birefringence corresponding to different extensions are very nearly proportional. The divergences at low extensions are due to the fact that the birefringence is affected not only by the total quantity of crystalline material but also by the orientation of the crystallites; it is only when the crystallites lie approximately in the direction of the extension (as they do at higher extensions) that the two methods would be expected to yield the same results quantitatively.

The important general conclusion to be drawn from these observations is that there is no essential difference between the processes involved in crystallization by extension and crystallization in the unstretched state. The effect of extension is simply to speed up the process, so that at the highest extension it is practically completed within one second.

VULCANIZED RUBBER

Bekkedahl[1] has studied crystallization in vulcanized rubber, using a dilatometer, with mercury as the confining liquid. He found that the density changes follow the same course as in raw rubber, but the rate of crystallization is slowed down to an increasing extent as the percentage of combined sulfur is increased, though the final amount of crystallization is not greatly affected. For a compound containing 0.5 per cent sulfur, the time for approximate completion of the process was 200 days, compared with 10 days for unvulcanized rubber. The melting temperature was, however, unaffected by vulcanization.

Hysteresis in Stress-strain Curve.—It is well known that the stress-strain curve of vulcanized rubber differs according to whether the extension is increasing or decreasing. Successive cycles of extension and retraction enclose a loop, representing an energy loss in the cycle. The area of this hysteresis loop is found to be smaller the higher the temperature. This effect is due largely (though not entirely) to crystallization.

A rather striking difference is observed in the retraction phenomena of raw and vulcanized rubber. Whereas in stretched raw rubber the crystalline state remains after removal of the stress, in vulcanized rubber removal of the stress is accompanied by immediate relaxation and disappearance of the crystalline phase. The difference, however, is only qualitative, for at low temperatures the extended (crystalline) state is stable, even in vulcanized rubber. The retraction temperature is reduced by about 13° C for every additional 1 per cent of combined sulfur. A test based on this property (T—50 test) has been used as a criterion of vulcanization[3].

X-RAY EVIDENCE

The most definite evidence on the existence of crystals in rubbers comes from the observation of the diffraction pattern produced by x-rays. There are four distinct types of pattern, associated with specific types of structure. These are the following:

(1) *Single Crystal.*—A single crystal, representing the highest state of ordered arrangement, gives a pattern of sharp spots, arranged in a geometrical order. From the analysis of the positions and intensities of the spots, the relative positions of the atoms in the structural "lattice" of the crystal can generally be calculated.

(2) *Powder (or Polycrystalline Solid).*—The powder, or polycrystalline solid, having crystal directions arranged at random, gives rise to a characteristic pattern of sharply defined circles. With very small sizes of crystallite the rings become diffused until ultimately the pattern approaches (3).

(3) *Liquid (or Glass).*—A liquid or glass is characterized by a more or less random arrangement of atoms. The only difference structurally between these two states is that in a glass the positions of the atoms are fixed, whereas in a liquid they are continually fluctuating. The x-ray diffraction pattern consists only of one or more broad haloes. These arise from the fact that, although the structure is random, there is nevertheless a tendency for certain interatomic distances to occur more frequently than others.

(4) *Fibres.*—Natural and artificial fibres (wool, silk, Nylon, etc.) give a type of spot pattern in which the number of spots is generally not so great as in (1), and the spots are arranged in a characteristic manner. There is also usually a diffuse background like that in (3). This type is due to the presence

of crystallites all oriented more or less along the fibre axis; together with a component of noncrystalline "amorphous" molecules. The analysis of the crystal structure is considerably more difficult than is the case with (1).

When we examine rubber in its various states we obtain the following results:

(a) Ordinary unstretched raw and vulcanized rubbers give the liquid pattern (3). This is consistent with our knowledge of the molecular structure of elastic rubber, discussed earlier. Rubber cooled rapidly to below −70° C and brought to the brittle or glassy state gives an identical pattern.

(b) Crystalline unstretched rubber gives a pattern of rings like (2) above. This is accompanied by a background of the type (3), showing the existence of a polycrystalline phase, together with an amorphous component.

(c) Stretched rubber gives the fibre pattern (4). The work of Field[4] suggests that, in the most highly stretched rubber, the proportion of the crystalline phase is about 80 per cent.

Various attempts have been made to determine the atomic structure of the crystal on the basis of the fibre pattern. So far, none of the proposed solutions has met with general acceptance.

MOLECULAR STRUCTURE OF CRYSTALLINE RUBBER

From the size of the spots in the x-ray fibre pattern, it is possible to estimate the size of the crystallites in crystalline rubber. They are found to have a length of about 600 Ångstrom units (6×10^{-6} cm.). The average length of a molecule in raw rubber being 20,000 Å. (0.0002 cm.), it follows that the average molecule must pass alternately through several crystallites. The structure of crystalline rubber must, therefore, be something like that represented in Figure 3; a number of separate crystallites tied together by lengths of molecules which cannot be fitted into a neighboring lattice, and which provide the amorphous component whose presence is always revealed by the x-ray photographs. On this model most of the physical phenomena associated with crystalline rubbers can be explained simply. Consider first the characteristic shape of the curves in Figures 1 and 2. A few adjacent portions of molecules come together spontaneously to form the nucleus of a crystal. This grows by accretion of other molecules at a rate which must increase as its surface area increases. This is why the rate of crystallization at first increases rapidly with time. A stage is then reached where the presence of neighboring crystallites so much impedes the freedom of movement of adjacent molecules that the rate of crystallization slows down and ultimately almost stops. But it never stops completely. The mutual entanglements of the "amorphous" molecules are slowly "shaken out", thus allowing of slight increases in the crystallite sizes over a long period of time. It is clear, however, that 100 per cent crystallization is impossible.

The effect of stretching is simply to force the molecules into a state of alignment in which less rearrangement is required for crystallization. The two phenomena, crystallization by freezing and crystallization by extension, are not two distinct processes, but a single process occurring under different physical conditions, between which a continuous gradation may be observed.

At sufficiently low temperatures the molecular mobility may be reduced to such an extent that crystallization does not occur in any reasonable time. That is why rubber cannot be crystallized at temperatures below −40° C.

By introducing permanent cross-links between the molecules, vulcanization reduces their mobility and thus slows down the rate of crystallization. Another aspect of this reduced mobility is the reduction or elimination of plastic flow which is associated with vulcanization.

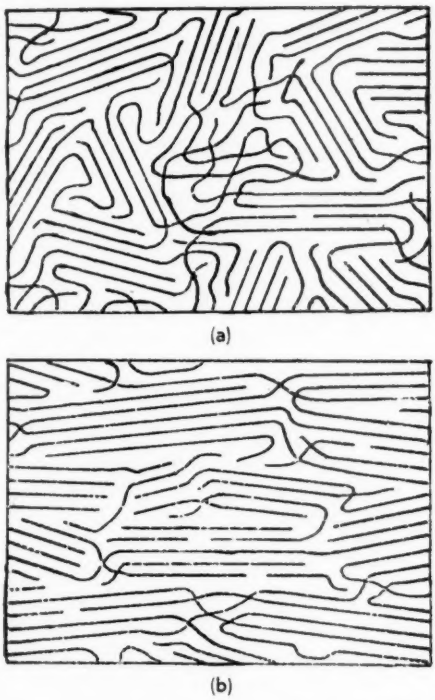

FIG. 3.—Molecular arrangements in crystalline rubber, (*a*) unstretched, (*b*) stretched. The parallel bundles represent crystallites.

MECHANICAL EFFECTS OF CRYSTALLIZATION

Since a number of molecules become locally associated in the crystallite, crystallization has the effect of introducing a kind of cross-linking between molecules, akin to vulcanization. The effect is strikingly exhibited in raw rubber, in which the rate of plastic deformation at first rises with increasing extension, then begins to fall again as the extension is further increased[5]. We conclude from this experiment that mechanical entanglements, which are responsible for the maintenance of the network structure of raw rubber, become of less importance at high extensions, where their function is taken over by the more effective binding of the molecules in the crystal lattices. The same effect is undoubtedly responsible for the very high tensile strength of vulcanized rubber. GR-S, which like all copolymers of irregular molecular structure cannot crystallize, has a very much lower tensile strength.

Highly stretched crystalline rubber possesses many of the characteristics of fibrous materials. It may readily be torn along the direction of the extension, but is extremely tough in directions at right angles. If frozen in liquid

air and hammered, it splits up along the fibre axes, in a similar manner to wood. We see here the direct effect of a structure consisting of oriented crystallites.

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SYSTEMS MANIFESTING SUPERPOSED ELASTIC AND VISCOUS BEHAVIOR *

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The theory of the mechanical behavior of deformable substances is divided into three parts. First, there is the geometrical problem of defining the state of strain in a body. This problem has been solved in terms of the strain tensor for the case of small deformations. Secondly, there is the dynamical problem of defining the state of stress in a body and of extending Newton's laws of motion to derive equations of motion and equilibrium for nonrigid matter. Finally, it is necessary to postulate relationships between the components of the strain tensor and the components of the stress tensor. It is this aspect alone which relates to the specific nature of the substance involved. The classical theory of elasticity, which in certain ranges of deformation, temperature, and frequency applies very closely to the mechanical behavior of crystalline solids, is characterized by the assumption of Hooke's law, which states that there is a linear relation between the components of stress and the components of strain. The classical theory of hydrodynamics, which applies very closely to the mechanical behavior of simple liquids and gases, is characterized by the assumption of Newton's viscosity law, which states that there in a linear relation between stress and rate of strain.

However, a very wide class of substances exhibits mechanical behavior in which elastic and viscous behavior are clearly superposed. Many of these substances, including rubbers, fibers, plastics, leathers, glasses, muscle tissue, and wood, are of great commercial or biological interest because of their complex mechanical behavior. The classical physicists, including illustrious men such as Maxwell and Boltzmann, were not unaware of the importance and theoretical interest attached to substances exhibiting superposed elastic and viscous behavior, and a classical theory for these phenomena was formulated.

Nearly a century ago Maxwell postulated an equation for one type of superposed elastic-viscous behavior, namely, the relaxation of stress in substances held at constant deformation, which phenomenon is particularly noticeable in substances such as pitch. The socalled Maxwell relaxation equation is:

$$\frac{ds}{dt} = \frac{1}{G}\frac{df}{dt} + \frac{1}{\eta}f \tag{1}$$

where ds/dt is the rate of strain, f the stress, G an elastic modulus, and η a coefficient of viscosity. This equation corresponds to a mechanical model consisting of a spring and dashpot in series which we shall henceforth call a Maxwell element. If the strain is held constant ($ds/dt = 0$), then the decay

* Reprinted from *The Journal of Chemical Physics*, Vol. 13, No. 1, pages 3–27, January 1945. This paper was presented at the Inaugural Meeting of the Division of High-Polymer Physics of the American Physical Society at Rochester, N. Y., June 23, 1944.

of stress at constant strain can be found by integrating Equation (1) giving:

$$f = f_0 e^{-t/\tau}; \quad \tau = \eta/G \tag{2}$$

where f_0 is the initial stress (at time $t = 0$) and τ, the relaxation time, is defined as above.

The mechanical model corresponding to Maxwell's relaxation equation and graphs of the stress decay function plotted against linear and against logarithmic time are shown in Figure 1.

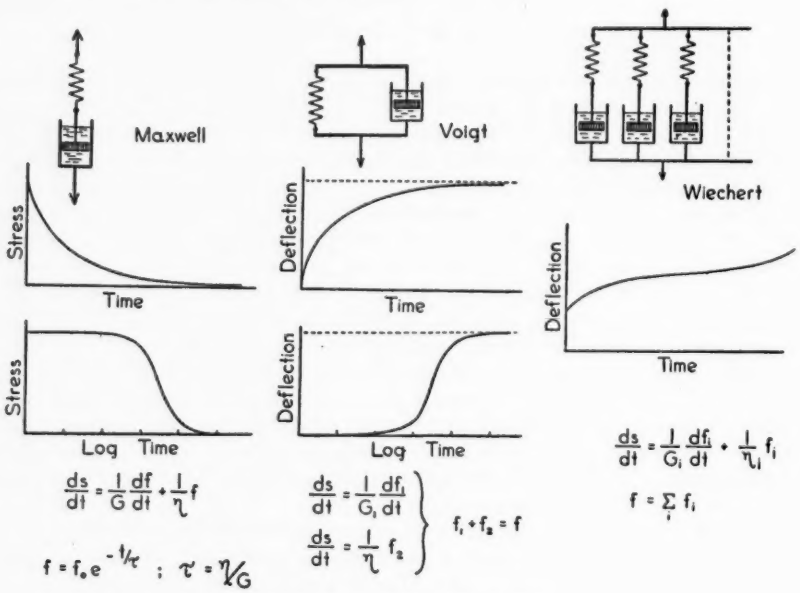


FIG. 1.—Mechanical models of matter.

The Maxwell theory is incomplete because it fails entirely to account for the phenomenon of creep under constant stress (or constant load). This behavior of matter can be readily paralleled by a mechanical model first introduced by Voigt, in which an elastic element (spring) and viscous element (dashpot) are placed in parallel. This, of course, corresponds to a linear differential equation for each element as shown in Figure 1, the stress dividing itself in each member in such a way that the rate of strain is the same in each. In Figure 1 are shown the differential equations corresponding to the Voigt model, and the deflection *vs.* time curves obtained from these equations. The Voigt theory is also incomplete because it does not account for relaxation of stress at constant elongation.

A theory that includes as special cases the results of the Maxwell and Voigt theories was proposed by Wiechert. The mechanical model suggested by Wiechert is simply a large number of Maxwell elements placed in parallel, as shown in Figure 1. Mathematically, this corresponds to a system of linear differential equations of the Maxwell type, the rate of strain in each equation being the same throughout the system, and each of the partial stresses in each equation being an aliquot portion of the total stress. Each equation can be

specified by a relaxation time, and in the general case an infinite number of Maxwell elements can be used by specifying a distribution of relaxation times.

It can be readily seen that this type of generalized theory can "explain" very complicated elastic-viscous behavior. However, the theory cannot be regarded as satisfactory without a sound molecular basis for interpreting the constants appearing in the equations in terms of the detailed structural theories of matter. Moreover, the assumptions concerning the linearity of the relations between stress and strain and stress and rate of strain need to be reëxamined.

New interest in problems of general rheology was awakened by the commercial development of synthetic rubbers, fibers, plastics, etc., the physical properties of which could be controlled by various polymerization methods. This, together with new information and theories concerning the structure of polymeric materials, led to attempts to give specific meaning to the "springs" and "dashpots" of the classical theory in terms of the structural features of particular substances. Among the workers in this field were W. Kuhn, H. Mark, H. Leaderman, R. Simha, P. Kobeko, A. Lazurkin, J. D. Ferry, and many others. Simultaneously a deeper insight into the nature of molecular relaxation processes was achieved through the work of P. Debye, L. Prandtl, R. Becker, J. Frenkel, H. Eyring, R. Barrer, and other workers. Finally, in the field of rubberlike or high elasticity, a sound approach was provided by the work of H. Mark, K. H. Meyer, E. Guth, H. M. James, F. T. Wall, L. R. G. Treloar, and P. J. Flory.

It is impossible to detail the work of the various writers and workers in the field of elastic-viscous phenomena. Furthermore, inasmuch as the subject is still in a stage of rapid development, it is not yet possible to attain a proper perspective of the field. For these reasons the following discussion will be restricted to work with which the authors have been directly connected: theoretical work of the senior author with Professor H. Eyring of Princeton University, and joint experimental-theoretical researches of both authors with J. H. Dillon and I. B. Prettyman of the Firestone Tire and Rubber Company, and R. B. Mesrobian and T. E. Allen of Princeton. The work of other authors is referred to only as it contributes directly to the single viewpoint adopted here.

ELASTIC-VISCOUS PROCESSES

The molecular processes that give rise to macroscopic elastic-viscous phenomena depend on the particular structural features of each new class of substances studied, but there are nevertheless certain underlying similarities in the elementary processes which are common to all condensed phases. It is necessary to idealize the situation and to assume that, in a body subjected to external stresses, there exist certain regions of elementary molecular movements and readjustments to the stresses that recur throughout the substance and are independent of the molecular movements in neighboring regions. We shall call the elementary process that occurs in such a region a "unit process of deformation", remembering that the motion of an atom, molecule, or group of atoms or molecules might be involved in this unit process. Figure 2 exemplifies the types of elastic-viscous processes that might occur in a crystalline solid and in substances such as rubber. Because of the external shearing stresses atom A in the crystal lattice might jump into the new position of equilibrium A', in addition to undergoing an immediate coherent change in the equilibrium distance to centers of neighboring atoms. It might also be that the unit process

of deformation involves the two atoms A and B simultaneously moving to a new position of equilibrium. Not all unit deformation processes in the substance are alike. For example, for atom C, which is not near a defect, to jump to a new position of equilibrium, a large scale reorientation of neighboring atoms is necessary. Atom C, however, moves relative to other atoms because of the elastic shift of all lattice distances in the crystal under the action of the external shearing stress.

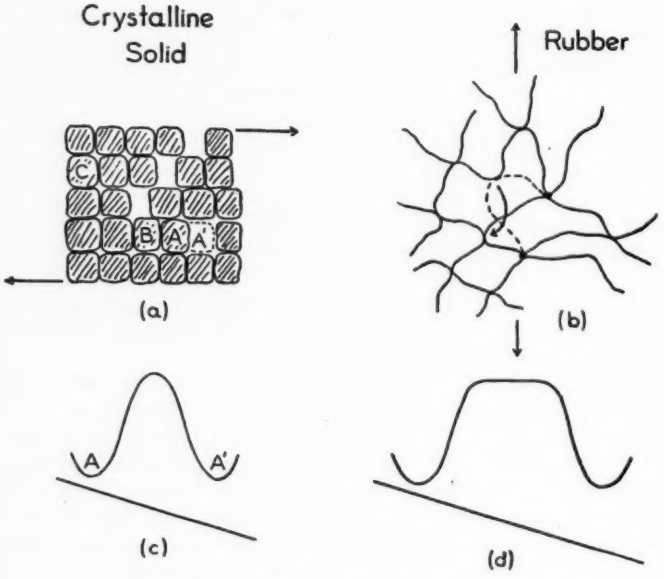


FIG. 2.—Elastic-viscous processes.

In Figure 2 is also shown a typical unit process that occurs in polymeric networks such as rubber. Here too the external stress acts in two ways: It tends to uncoil elastically the portions of the molecular chains between network junctures, and at the same time it tends to cause a breaking and reforming in relaxed positions of the network junctures which are formed by secondary bonds between the chains.

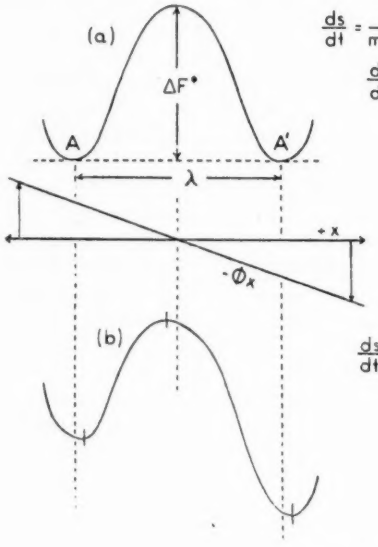
For a quantitative formulation of the elastic-viscous behavior represented by a unit process of deformation, we imagine the atom or group of atoms involved in the unit process to be momentarily at rest and consider the free energy surface on which this atom or group of atoms moves. This free energy surface, shown in Figure 2(c), arises, of course, from the interaction with neighboring atoms. At the instant under consideration the deformation unit is at equilibrium at point A and, therefore, occupies a minimum position in a free energy well. At point A' another position of equilibrium is available and, therefore, point A' corresponds to another minimum in the free energy surface. Between A and A' the deformation unit must move through energetically unfavorable configurations which correspond to a free energy hill. The effect of stress is to subtract a linear potential gradient from the original free energy configuration.

UNIT PROCESS OF DEFORMATION

Consider a molecule at equilibrium in a potential well at point A next to a new equilibrium position at point A' (see Figure 3). The potential curve will for mathematical simplicity first be assumed to be of the form:

$$\frac{\Delta F^{\ddagger}}{2}\left(1-\cos\frac{2\pi x}{\lambda}\right) \tag{3}$$

so that $\Delta F^{\ddagger}$ is the free energy of activation for movement from one equilibrium position to the next and λ is the distance between successive equilibrium positions. The coördinate x is taken in the direction in which the local force



$$\frac{ds}{dt}=\frac{1}{m\lambda_1}\frac{d\Phi}{dt}+\frac{\lambda}{\lambda_1}k'\left[\exp\left\{\frac{\alpha\Phi\lambda}{kT}\right\}-\exp\left\{\frac{(1-\alpha)\Phi\lambda}{kT}\right\}\right]$$

$$\frac{ds}{dt}=\frac{1}{m\lambda_1}\frac{d\Phi}{dt}+\frac{\lambda}{\lambda_1}k'\,2\sinh\frac{\Phi\lambda}{2kT}$$

$$\Phi=\frac{f}{N}\qquad k'=\frac{kT}{h}e^{-\Delta F^{*}/kT}$$

$$\frac{ds}{dt}=\frac{1}{mN\lambda}\frac{df}{dt}+\frac{\lambda}{\lambda_1}k'\,2\sinh\frac{f\lambda}{2NkT}$$

$$\frac{ds}{dt}=\frac{1}{G}\frac{df}{dt}+\frac{1}{\eta}f$$

FIG. 3.—Unit process of deformation.

owing to the field of external stresses is acting. The effect of this force is to add a linear term, $-\phi x$, to the potential surface in which the molecule moves, where ϕ is the local force and x is the distance. The new potential surface after addition of the stress gradient is shown in Figure 3(b).

The rate of deformation is given by the sum of two terms. In the first place, the unit at A, under the action of stress, shifts its position in the free energy well to a new position of equilibrium at B. This shift occurs in phase with the stress, and is the elastic component of the deformation. The amount of elastic shift is related to the curvature of the free energy well.

Secondly, there is a jumping over the barrier from A to A' as well as in the opposite direction. The free energy of activation in the forward direction is less than that in the backward direction, as shown in Figure 3(b). The resulting net rate of flow in the forward direction also contributes to the rate of shearing[1].

In a previous publication[2] it was shown that the rate of strain resulting from the local force could be calculated exactly from the potential curve (3).

The resulting expression is:

$$\frac{ds}{dt} = \frac{\lambda^2}{2\pi^2\lambda_1\Delta F^{\neq}}\frac{d\phi}{dt} + \frac{\lambda^2 e^{-\Delta F^{\neq}/kT}}{\lambda_1 h} 2 \sinh \frac{\phi\lambda}{2kT} \tag{4}$$

where ds/dt is the rate of strain, k is Boltzmann's constant, h is Planck's constant, and λ_1 is the root mean square distance between identical deformation units projected in a direction perpendicular to the plane over which the stress is considered.

For a more general free energy surface, which is, nevertheless, of the same general shape as shown in Figure 3, the rate of strain is given by:

$$\frac{ds}{dt} = \frac{1}{m\lambda_1}\frac{d\phi}{dt} + \frac{\lambda}{\lambda_1} k' 2 \sinh \frac{\phi\lambda}{2kT} \tag{5}$$

where

$$k' = \frac{kT}{h} e^{-\Delta F^{\neq}/RT}$$

where m is the curvature of the potential barrier near the minimum. It is to be observed that m is the force constant describing the interaction between molecules. It is clear that the first term on the right in Equation (5) represents an elastic deformation, while the second term is a term representing flow.

In actual substances the structural features are such that we can classify together a number of unit processes of deformation, calling these processes of type i. Let there be ν_i such processes per unit volume. In general we wish to consider the effect of stress across a given plane of the medium. The direction perpendicular to this plane is taken as the Z direction, and the total stress localized on the ith type of units is called f_i.

Let the root mean square value of the projected distance along the Z axis between neighboring regions where processes of type i are occurring be λ_{1i}. Then it may be assumed that the local force on each process of type i is given by:

$$\phi = \frac{f_i}{N_i}, \quad \text{where} \quad N_i = \nu_i\lambda_{1i} \tag{6}$$

This assumption is valid if the total stress on each of the ith type of deformation units is distributed uniformly among these units.

Having established the very general rheological equations for the unit process of deformation, it remains necessary to specify the manner in which the external stress divides between various units, and how the macroscopic rate of strain is related to the rate of strain for the deformation units. For this the reasonable assumption is made that the medium retains the identity of its microscopic features under stress or deformation; in other words, it is assumed that the stress divides itself among the deformation units in such a way that the rate of strain is the same for each and equal to the macroscopic rate of strain. This is equivalent to the basic assumption of the Wiechert model. The general elastic-viscous equations from Equations (5) and (6) are:

$$\frac{ds}{dt} = \frac{1}{m_i\lambda_{1i}}\frac{d\phi_i}{dt} + \frac{\lambda}{\lambda_1} k' 2 \sinh \frac{\phi_i\lambda_i}{2kT} \quad i = 1, 2, 3, \cdots \tag{7}$$

where

$$\phi_i = f_i/N_i; \quad f = \sum_i f_i$$

and

$$k' = \frac{kT}{h} e^{-\Delta F^{\ddagger}/RT}$$

The symbols have been defined in the previous section; the subscript i refers to the ith type of unit process of deformation.

The theory presented here is, therefore, similar to the Maxwell-Wiechert theory. The chief differences lie in the fact that a nonlinear flow term which becomes linear under the condition of small internal stress fields replaces the linear Newtonian flow term in Maxwell's equation, and the constants appearing in the equation are given specific molecular interpretation.

PHYSICAL PROPERTIES OF RUBBERLIKE MATERIALS

The general theory of superposed elastic-viscous behavior of matter presented in the previous sections must be supplemented by a detailed picture of the structural properties of the particular class of substances under consideration if useful application of the theory is to be made. In the remainder of this article we shall devote our discussion to polymeric materials in the rubbery state of aggregation—particularly natural and synthetic rubbers. These materials are characterized both by a long range and by a local structure. The long-range structure is a polymeric network, the network junctures being composed of sparsely-occurring bonds between the coiled polymeric chains. These bonds may be primary cross-links, or secondary interchain bonds, such as dipole-dipole bonds or regions of local crystallinity. The portions of the network connecting contiguous network junctures are called network "chains". The local structure of the network is very similar to the local structure of liquids, the segments of the long chain molecules being in continual, fairly rapid motion, moving from one equilibrium position to the next. It is desirable to construct a theory of the overall physical properties based on molecular quantities such as the number of network junctures of a given type per unit volume, the strength of these cross-linking bonds, and the internal viscosity of the local liquidlike structure[3].

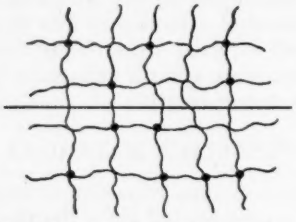
To find the relations between rate of strain, stress, and rate of stress over a given plane direction in a deformed rubberlike material we imagine a planar cut passing through the material in that plane. This cut passes through a large number of network chains, some of which are terminated by primary cross-links and others by secondary cross-links. Let us denote by N_1 the number of chains (henceforth called primary network chains) terminated by primary cross-links per unit area of the planar cut, and let N_2 denote the number of chains (henceforth called secondary network chains) terminated by secondary cross-links per unit area of the planar cut. In general there may be more than one type of secondary cross-link, so that classifying all secondary network chains together is a simplification. If s_1 and s_2 are the number of primary and of secondary network chains per unit volume, respectively, then n_1 and n_2, where:

$$n_1 = s_1/N_1; \quad n_2 = s_2/N_2$$

are the reciprocal lengths between primary cross-links and secondary cross-links in the direction perpendicular to the planar cut.

The structural features described above are the deformation units in terms of which the elastic-viscous properties of these substances must be explained. The equations of motion for pure tension or pure shear for primary network

chains and for secondary network chains in terms of the defined molecular quantities are shown in Figure 4. The elastic term in these equations represents the uncoiling of network chains assuming that the terminal points (cross-links) remain relatively fixed. The flow terms represent the contribution to the rate of deformation of rupturing processes at primary bonds along the chain which break the chains loose, and slipping processes occurring at the



$$f = f_1 + f_2 + f_3$$

Primary Network Chains:

$$\frac{ds}{dt} = \frac{1}{G_1}\frac{df_1}{dt} + n_1\lambda k_1' e^{f_1\lambda/2N_1kT}$$

Secondary network chains (interchain forces):

$$\frac{ds}{dt} = \frac{1}{G_2}\frac{df_2}{dt} + n_2\lambda k_2' 2\sinh\frac{f_2\lambda}{2N_2kT}$$

Segment motion (intrachain forces):

$$\frac{ds}{dt} = \frac{1}{G_3}\frac{df_3}{dt} + \frac{1}{\eta_3}f_3$$

FIG. 4.—Mechanical behavior of polymers.

secondary cross bonds. The specific rate constants which appear in the equations of motion for primary network chains and for secondary network chains are defined by:

$$k_1' = \frac{kT}{h}\exp\left(-\Delta F_1^{\ddagger}/RT\right)$$

$$k_2' = \frac{kT}{h}\exp\left(-\Delta F_2^{\ddagger}/RT\right)$$

where $\Delta F_1^{\ddagger}$ is the free energy of activation for the rupture of primary bonds, and $\Delta F_2^{\ddagger}$ is the free energy of activation for the breaking of secondary bonds. Generalization of these equations of motion to three-dimensional stresses and strains can be carried out readily.

A third type of unit process of deformation is included to account for the intrachain motion of chain segments. These motions are such that the local environment of chain segments resembles the environment of molecules in the liquid state. This motion has a damping effect on the motion of the primary and secondary network chains as a whole, much as if a viscous liquid were pervading the network structure of the polymeric substance.

STATISTICAL THEORY OF ELASTICITY FOR RUBBER NETWORKS

The "high elasticity" of rubberlike substances is caused by the fact that under stress the "chains" between network junctures can uncoil[4]. In rubbers, for certain regions of temperature, the chains are very mobile and, as we shall see, there is evidence that the internal energy of the network does not change as the network is stretched. The resistance to stretch is, therefore, caused by a decrease in entropy on stretching, and this in turn is caused by the fact that the network chains can assume many more conformations in the unstretched state, where the distance between network junctures is small, than in the stretched state, where the distance between network junctures is larger.

From thermodynamics we can immediately derive the law:

$$f = \left(\frac{\partial E}{\partial l}\right)_T - T\left(\frac{\partial S}{\partial l}\right)_T \tag{8}$$

where f is tension, l represents length, E is internal energy, S is entropy, and T is temperature. Inasmuch as the first term on the right-hand side of Equation (8) is taken equal to zero, the equation of state can be derived if we can relate S to l. This is done by relating S to the probability P by Boltzmann's relation:

$$S - S_0 = k \ln P/P_0 \tag{9}$$

where P/P_0 represents the ratio of the probabilities (or ratio of total number of available configurations) for the stretched and unstretched networks.

The evaluation of the probabilities P and P_0 is accomplished by determining the number of ways that a coiling hydrocarbon chain can assume a projected length x between its ends along any direction in space. The stable configuration for successive bond directions is believed to be the staggered configuration. The meanderings of a hydrocarbon chain can be described as a continuous path on a diamond lattice, each path being equally likely if we neglect the effect of steric hindrance.

Suppose that the total number of carbon-carbon bonds in the chain is n, and the bond length divided by $\sqrt{3}$ is taken as the unit of length. The problem of the random walk on a diamond lattice turns out to be equivalent to the problem of finding the distribution in heads of a penny that is being tossed n times and has a $\frac{2}{3}$ probability of repeating its last flip.

The result of a rather lengthy calculation[2] is that the probability of a chain of n bonds having the projected length x along any direction in space is:

$$p_n(x) = \frac{1}{2\sqrt{\pi n}} \exp\left(-x^2/4n\right) \tag{10}$$

This formula can be directly applied to the case where "ends" of the hydrocarbon chain are successive juncture points in a polymer network. It is assumed that, on stretching, there is a homogeneous change in the components of distance between successive network junctures throughout the rubber which is the same as the change in dimensions of the macroscopic sample. By averaging over all orientations and over all chains of the network, P/P_0 in Equation (9) can be evaluated, and thereby the stress-strain curve at equilibrium can be derived[4]. The result is:

$$f = skT\left\{\frac{l}{l_u} - \left(\frac{l_u}{l}\right)^2\right\} \tag{11}$$

where l_u represents unstretched length, l the equilibrium length at tension f, and s the number of network chains of all kinds per cc. that remain unbroken and unrelaxed at the time of measurement.

The values of the elastic moduli G_1 and G_2 appearing in the equations of Figure 4 can be expressed as follows from Equation (11):

$$G_1 = 3s_1kT \tag{12}$$

$$G_2 = 3s_2kT \tag{13}$$

where s_1 and s_2 are as defined above: the number of primary network chains per cc. and the number of secondary network chains per cc., respectively. G_3 appearing in Figure 4 is an ordinary elastic modulus for crystalline substances (the modulus in the case that the temperature is sufficiently low for segment motion to be completely frozen). Usually G_1 has a magnitude of about 10^6–10^7 dynes per sq. cm. for soft rubber, whereas G_3 is of the order of magnitude of 10^{11} dynes per sq. cm.

We have presented above a theory based on *a priori* considerations concerning stress-strain relationships and on several assumptions regarding the structural characteristics of rubberlike polymers. In the succeeding sections we shall show how experimental results bear on this theory, and also how these results suggest modifications and extensions of the theory.

STRESS-TEMPERATURE-TIME RELATIONS FOR NATURAL AND SYNTHETIC RUBBERS

An equation has been given in the previous section which relates the stress and the elongation of a rubber sample in terms of the concentration of network chains in the rubber and the temperature, as follows:

$$f = skT\left\{\frac{l}{l_u} - \left(\frac{l_u}{l}\right)^2\right\} \tag{14}$$

where f is the stress (calculated on original cross-section), s the number of network chains per cc. of rubber, k Boltzmann's constant, T the absolute temperature, l the stretched length, and l_u the unstretched length of the sample. Thus, according to this equation, any changes in the stress of a rubber sample held at constant temperature and constant elongation must be caused by changes in the number of network chains s per unit volume of the rubber that are effective in maintaining the stress. As can be seen from Equation (14), changes in s can be measured in two ways: (1) one may keep the elongation l constant and measure the changes in f, or (2) one may keep f constant and measure the changes in l. The first method is referred to as "stress relaxation at constant elongation" and the second method as "tensile creep under constant load". Both types of measurement can be made in two different ways: First, one can keep the sample continuously elongated, or under load, as the case may be—this will be called the "continuous" method; or, one can elongate the sample or apply the load only momentarily when a measurement is taken, allowing the sample to remain unstretched at all other times—this will be called the "intermittent" method. Certain fundamental differences exist between the continuous and intermittent types of measurement, as will appear in the subsequent discussion.

Measurements of stress as a function of time in rubber samples held at constant elongation ("continuous relaxation"), using a variety of different rubber types, and made over a wide range of temperatures[5], have indicated that, for both natural and synthetic rubbers, three general temperature regions can be distinguished: (1) a low-temperature region of rapid change of stress with time, (2) an intermediate-temperature region in which there is practically no change in stress with time, (3) a high-temperature region in which there is again a marked decay of stress with time.

The low-temperature region is the region in which stiffening of the rubber is observed because of the stability of secondary bonds (van der Waals bonds) between network chains. The relaxation of stress occurring in this region has

been postulated as owing to the relaxing of these secondary bonds in the network structure (such as dipole-dipole bonds, etc.) which are partially stable during experimental times (roughly from 10 seconds to 10 hours) in that temperature range, and thus are able to contribute to the stress. The secondary bonds supposedly break and then reform in new, unstressed positions (where they no longer contribute to the stress) so that the changes occurring in the rubber during secondary bond relaxation are "reversible", and there is no permanent change in the rubber.

The high-temperature region of instability of stress with time is that temperature region associated with "heat aging" phenomena—softening and hardening which permanently destroy the rubbery properties of the material. The relaxation of stress in this region is attributed to a definite chemical reaction

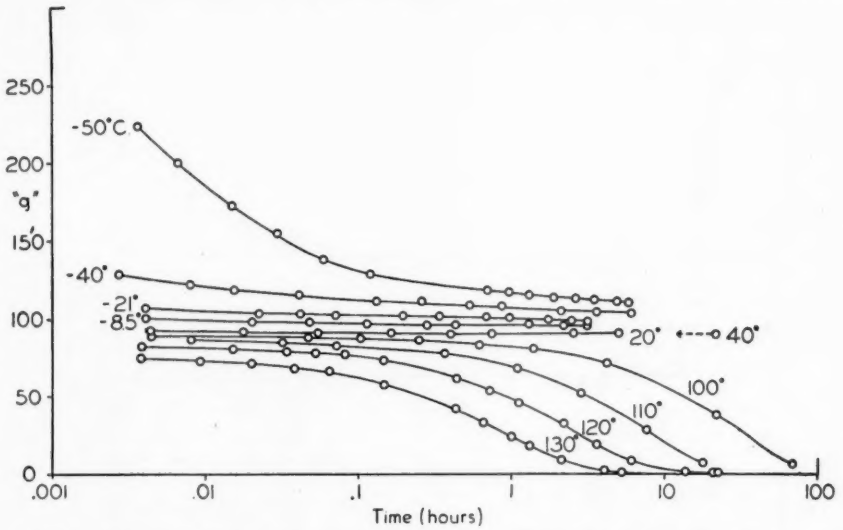


FIG. 5.—"g" as a function of time for various temperatures; Hevea gum, 50 per cent elongation.

which cuts chains by breaking primary valence bonds in the network structure; thus the changes in the rubber accompanying the relaxation of stress in this temperature region are not reversible, but cause a permanent deterioration of the network structure. This chemical scission reaction has been shown to require the presence of oxygen to occur, but only a slight amount of oxygen was found to be necessary.

In the intermediate-temperature region secondary bonds are so unstable that they have all relaxed by the time the first stress reading can be taken, and the primary bond scission reaction occurs so slowly that it produces no noticeable effect during the experimental time. It is in this intermediate temperature region of relative thermodynamic stability that statistical and kinetic treatments of rubber elasticity, which do not take time effects into account, have their greatest validity.

If experiments could be carried out at low enough temperatures, one might expect to find a fourth temperature region—a very low temperature region where secondary bonds as well as primary bonds would be completely stable

within experimental times, and therefore there would be no change in stress with time.

The first three temperature regions mentioned above can be seen in Figure 5, where continuous relaxation data for Hevea gum over the temperature range $-50°$ to $+130°$ C are shown[6]. It will be noted that reduced stress, "g", has been plotted as the ordinate rather than the stress itself. The reason for this is that at a fixed elongation the stress is presumably proportional to the absolute temperature T as well as to the concentration of chains in the network s, as is seen from Equation (14). Thus by eliminating the effect of temperature by "reducing" the stress values arbitrarily to 25° C, *i.e.*, the stress f is multiplied by $298/T$ at each temperature T to give "g", the stress values at different temperatures are then directly comparable in terms of s.

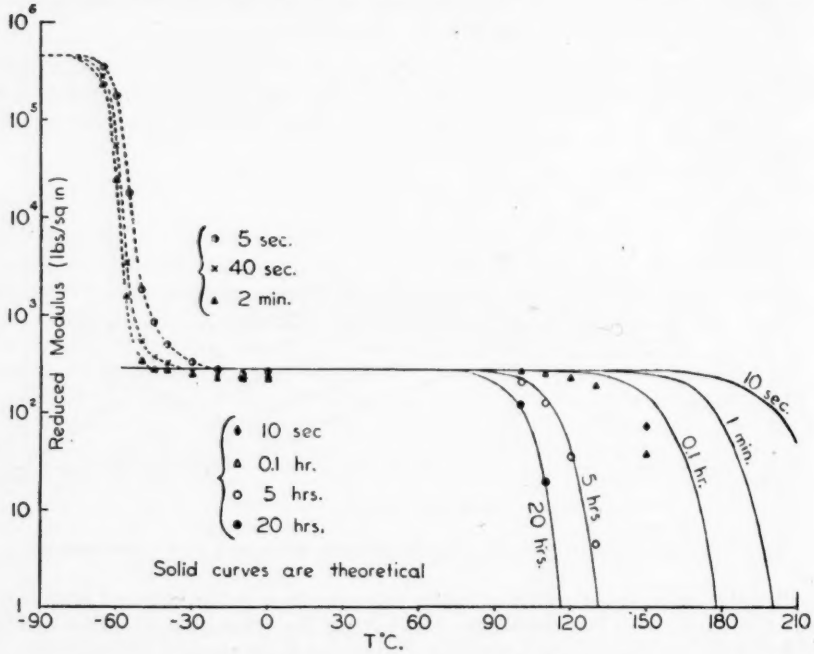


FIG. 6.—Reduced modulus *vs.* temperature, Hevea gum.

There is considerable decay of stress observed in the low and high temperature data, whereas in an intermediate temperature range there is little change in stress with time. This is seen even more clearly in Figure 6 where "reduced modulus" (modulus times $298/T$) at different fixed times is plotted against temperature. The ordinate could be changed to reduced stress simply by relabelling the ordinate scale (reduced modulus = 2.985 × reduced stress). The fact that the reduced modulus remains the same in this temperature range of stability means, of course, that the stress f is directly proportional to absolute temperature in this range. From this fact it can be proved thermodynamically that the assumption, made in all kinetic theories of rubber elasticity, that the internal energy does not change when the rubber is stretched, is correct.

Consider the thermodynamic relation:

$$\left(\frac{\partial E}{\partial l}\right)_T = -T\left(\frac{\partial f}{\partial T}\right)_l + f \tag{15}$$

If f is directly proportional to T, then, by substituting in Equation (15), obviously $(\partial E/\partial l)_T$ is equal to zero.

The experimental data in this graph were obtained from two sources. The data at 0° C and below were obtained from what might be considered a modified form of continuous creep experiment which measures modulus as a function of time. The experimental method, which has been described elsewhere[7],

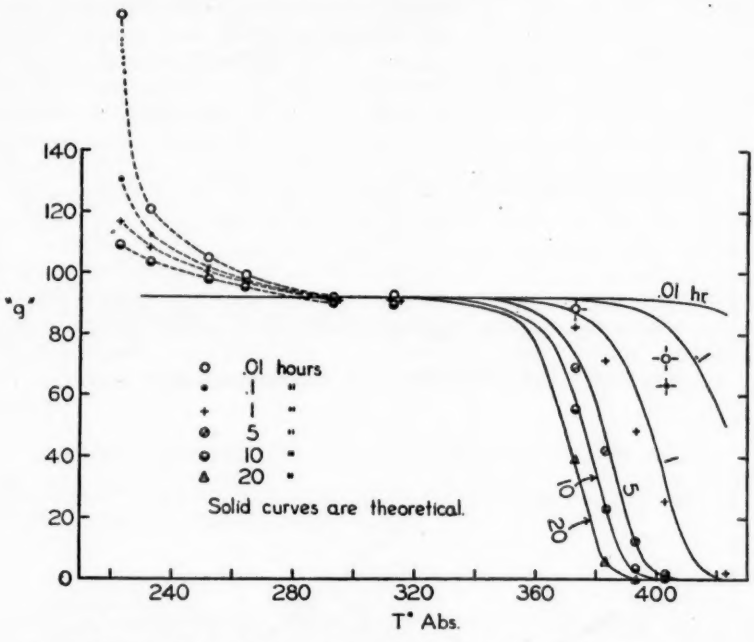


FIG. 7.—"g" as a function of temperature for various times, Hevea gum.

measures the bending of a horizontal bar sample, supported at the ends and with a weight applied in the center, as a function of time. These modulus data are undoubtedly not completely comparable with continuous relaxation data, although the 5-second modulus points should correspond at least roughly to the 5-second stress relaxation values. The modulus data were used here because they extend down to −65° C, where the effect of secondary bonds becomes very important in Hevea gum, and the modulus data give some idea of the magnitude of the secondary bond effect[8]. Dotted curves have been drawn through the experimental points and extrapolated to a maximum flat value toward which the points seem to be converging. This flat would be expected to extend all the way down to 0° K. In this very low temperature region (−273° C to about −75° C) the effect of secondary bonds is so predominant that, if the flat value is approximately correct, less than a tenth of one per cent of the stress is to be attributed to primary bonds in the network,

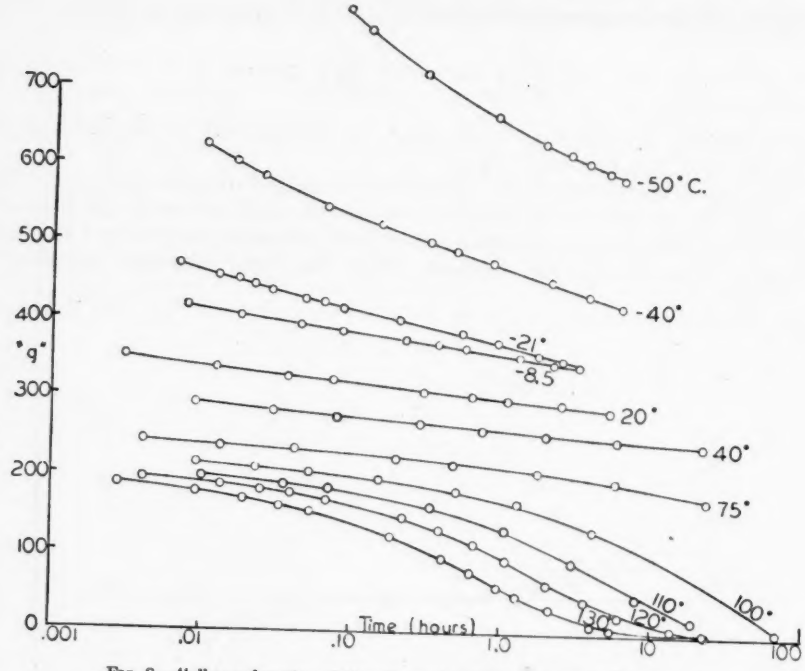


FIG. 8.—"g" as a function of time for various temperatures, Hevea tread.

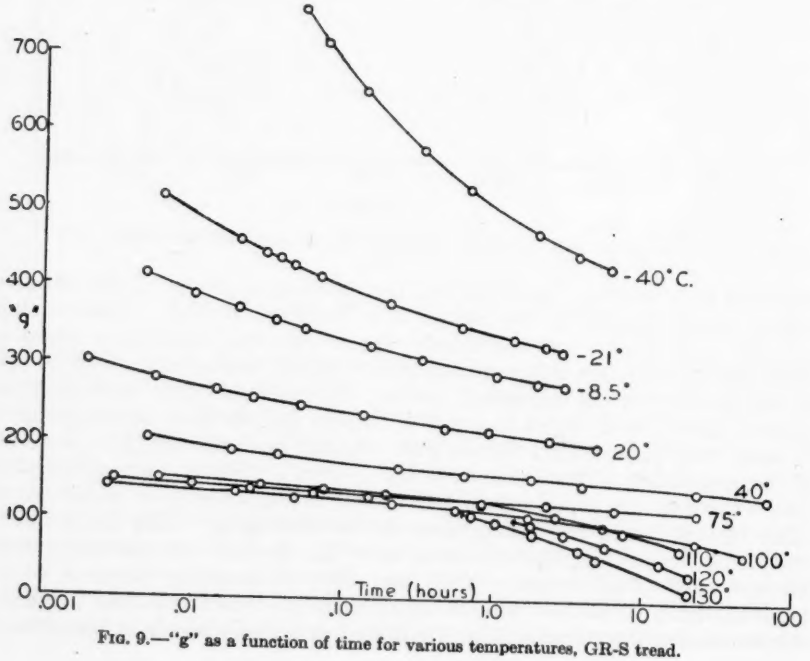


FIG. 9.—"g" as a function of time for various temperatures, GR-S tread.

all the rest being caused by secondary bonds. In this temperature region the rubber is essentially a crystalline solid, and shows no rubbery properties whatever.

The high temperature experimental points were taken from the stress relaxation curves of Figure 5. The solid curves drawn to accompany the high-temperature data were calculated theoretically from Equation (16), which will be discussed later. It is seen that they agree excellently with the 5-hour and 20-hour experimental points. Figure 7, which is replotted entirely from the data of Figure 5, shows essentially the same points of interest as Figure 6. The thing particularly to be noticed in these graphs is the clear separation between the three (possibly four) temperature regions which have been discussed, particularly the intermediate temperature region of stability of stress (or modulus) with time, which is clearly set off from the low and high temperature regions of instability, and which extends from about $-10°$ C to $+75°$ C.

In Figures 8 and 9, stress relaxation data for Hevea tread and GR-S tread are shown for the temperature range $-50°$ to $+130°$ C (the $-50°$ curve for GR-S tread is not shown because the "g" values are too high to appear on the graph). In Figures 10 and 11 the data from Figures 8 and 9 are replotted as "g" *vs.* temperature at different fixed times. The most striking thing to be noticed in these latter graphs is that, in these rubber stocks, the secondary bond relaxation region overlaps the primary bond relaxation region to a much greater extent than is the case for Hevea gum. There is no temperature region in which the stress does not change with time. However, one can distinguish a roughly defined region where the stress does not change greatly with time. This is the general rule rather than the exception; Hevea gum is unique among those rubbers studied in its wide, clearly defined temperature region of stress stability.

HIGH TEMPERATURE PRIMARY BOND PHENOMENA

The high-temperature stress-relaxation curves of Hevea gum are found to fit the simple unimolecular rate law:

$$f = f_0 e^{-k't} \tag{16}$$

where k' is of course the rate constant of the process, f is the stress at time t, and f_0 is the initial stress. The dependence of the relaxation rate on temperature is given by the equation:

$$k' = \frac{kT}{h} e^{-\Delta F^{\ddagger}/RT} = \frac{kT}{h} e^{-\Delta H^{\ddagger}/RT} e^{\Delta S^{\ddagger}/R} \tag{17}$$

where k is Boltzmann's constant, T the absolute temperature, h Planck's constant, R the gas constant, $\Delta F^{\ddagger}$ the free energy of activation, and $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ the heat and entropy of activation, respectively. It is found, in fitting the experimental curves of Hevea gum, that $\Delta F^{\ddagger} = 30.4$ kcal., and that the free energy of activation is entirely heat of activation, $\Delta S^{\ddagger}$ being equal to zero. The success with which the experimental data can be fitted with Equation (16) and (17), taking $\Delta F^{\ddagger}$ equal to 30.4 kcal., is seen in Figure 12, where experimental points and calculated curves are shown for Hevea gum at 100°, 110°, 120°, and 130° C.

Of all the various natural and synthetic rubbers studied, Hevea gum is the only rubber whose relaxation of stress curve follows the simple unimolecular

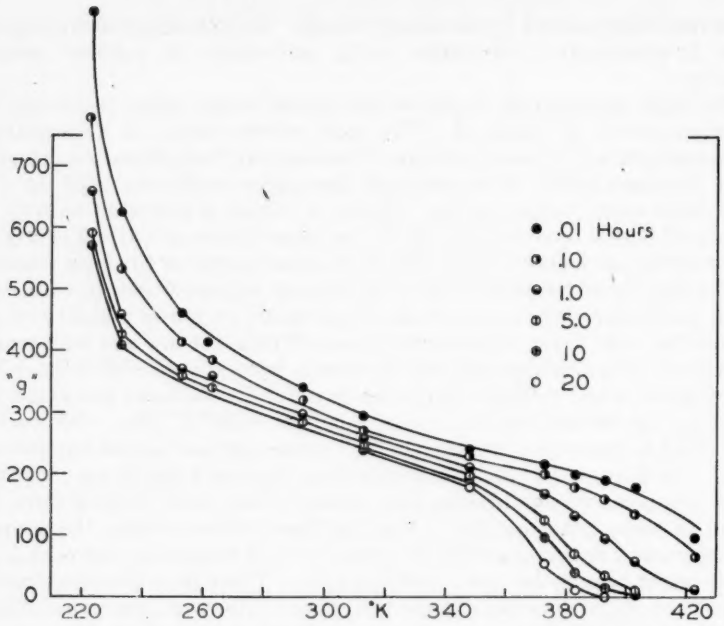


FIG. 10.—"g" as a function of temperature for various times, Hevea tread.

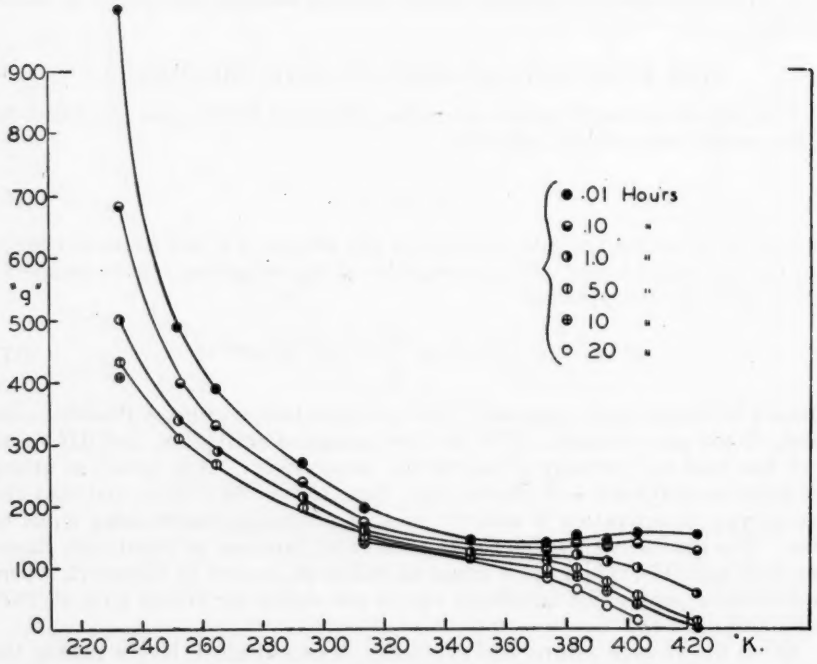


FIG. 11.—"g" as a function of temperature for various times, GR-S tread.

decay law (16). Nevertheless, if the "relaxation rate constant" k' of these other rubbers at any temperature is taken as the reciprocal of the time at which $f/f_0 = e^{-1} = 1/e$ [as is properly true only of rubbers obeying Equation (16)], it is found that the temperature dependence of the "rate" is given by Equation (17), just as for Hevea gum. The values of $\Delta F^{\ddagger}$ obtained for these

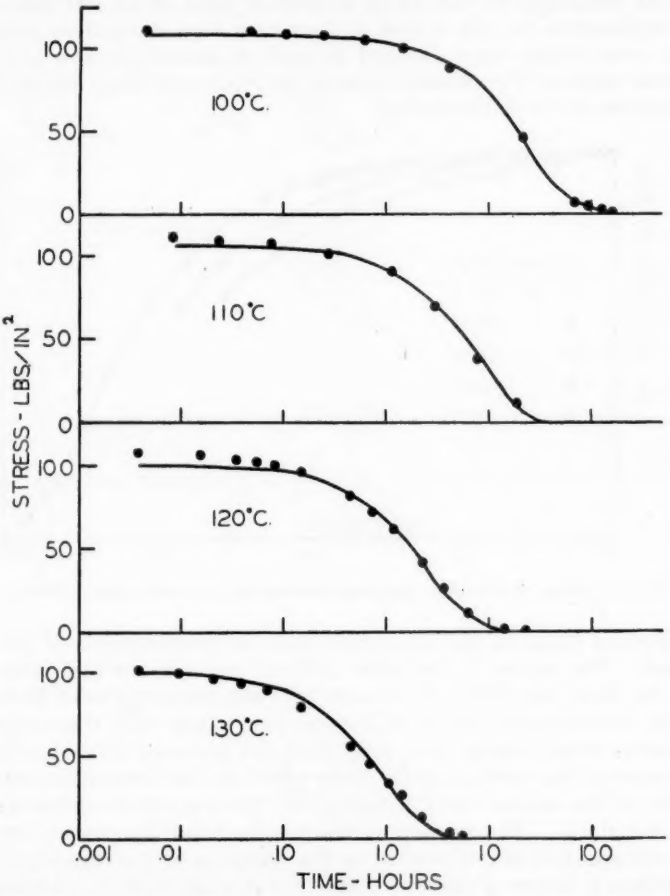


FIG. 12.—Hevea gum stock; 50 percentage elongation, theoretical curves, experimental points.

various rubbers all fall within the range 30.4 ± 2.0 kcal., with $\Delta S^{\ddagger}$ again equal to zero; and although these differences correspond to large practical differences in relaxation rates, the fact that $\Delta F^{\ddagger}$ is about the same in all cases suggests that the mechanism of relaxation is of the same type in all. As mentioned before, this high-temperature relaxation mechanism has been shown to be a scission process occurring in the presence of oxygen. By carrying out the relaxation experiments in purified nitrogen (highly oxygen-free), the relaxation rates of both natural and synthetic rubbers could be reduced about 1000-fold. Also, in a continuous creep experiment on a natural rubber stock, carried out at 110° C in a vacuum of 10^{-5} mm. of mercury, the creep rate was perhaps a thousand times less than that observed in air at the same temperature.

The effect of elongation on the relaxation rate is illustrated for Hevea gum in Figure 13. It is seen that in the range of 20 per cent to 100 per cent elongation, the relaxation curves obtained are identical (the five curves have been set equal at 0.01 hour to facilitate comparison), showing that elongation has no effect in this range. However, at 400 per cent and 700 per cent elongation, the rate of relaxation is seen to be increased, most so at 700 per cent. A possible explanation for this is that at these very high elongations some of the molecular chains may have uncoiled to their maximum possible extent, and the valence angles of the carbon atoms in the chains are being strained, which makes it easier to break the chains.

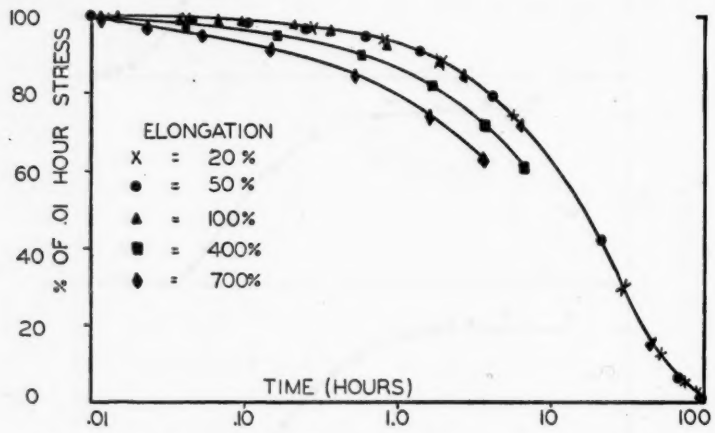


FIG. 13.—Effect of percentage elongation on relaxation rate; Hevea gum —100° C.

The general shape of the relaxation curve is characteristic of the rubber being used. The curves of the other rubbers are in every case more spread out in a log time plot than the unimolecular relaxation curve of Hevea. By comparing the relaxation curves of various gum stocks with the curves of the corresponding tread stocks, one finds that the presence of carbon black in the vulcanizate has comparatively little effect on the relaxation rate. The main effect of the carbon black is to increase the magnitude of the stress (see Figures 14 and 15). The relaxation rate can be definitely slowed down, however, by the addition of antioxidant to the vulcanizate, the difference in rates being perhaps a factor of three or four. On the other hand, changing from sulfur to nonsulfur cures does not markedly affect the relaxation curves.

After this brief discussion of the main characteristics of relaxation curves obtained by the "continuous" method (constant elongation), we now turn to a consideration of "intermittent" relaxation curves. These intermittent stress relaxation measurements are really simply periodic measurements of the modulus of the sample, and the curve obtained could be called a "modulus *vs.* time" curve instead of an "intermittent stress relaxation" curve if one so desired. The thing immediately noticed in examining the intermittent relaxation curves is that the intermittent curve differs markedly from the continuous curve of the same rubber (see Figures 14 and 15). In the continuous relaxation curves the stress always decreases continuously, and eventually reaches zero if the experiment is carried out for a long enough time. In the intermittent curves

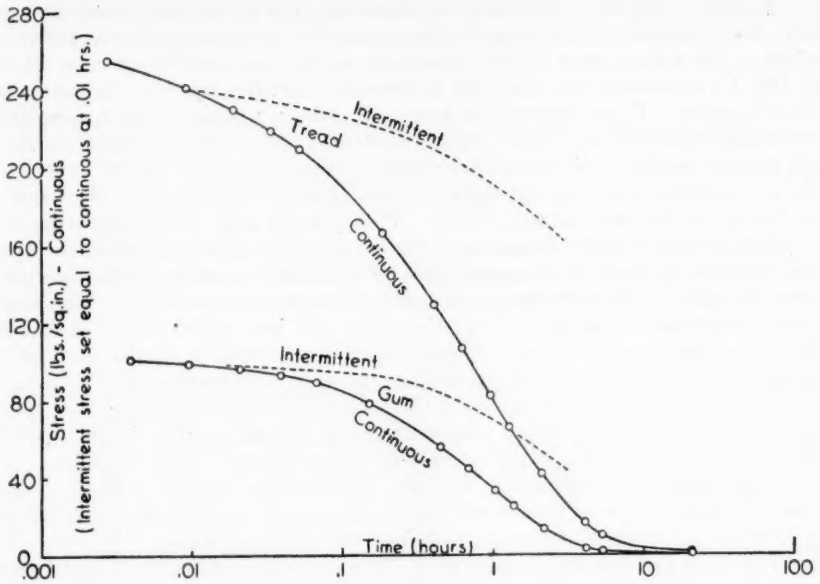


FIG. 14.—Continuous and intermittent stress relaxation; 50 per cent elongation; 130° C; Hevea stocks.

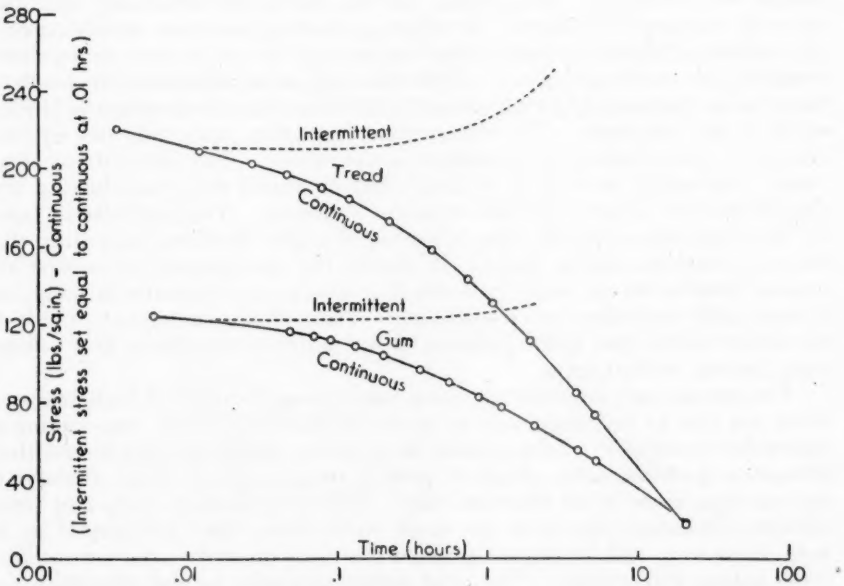


FIG. 15.—Continuous and intermittent stress relaxation; 50 per cent elongation; 130° C; GR-S stocks.

a remarkable variety of behavior is observed: The stress may decrease regularly, or increase regularly from the beginning; the stress may remain practically constant for a time, then begin to increase, or decrease; and in one case (Hevea at 100° C) the stress was observed to decrease initially, reach a minimum, and then increase. It is observed, in comparing the continuous and intermittent relaxation curves of any rubber, that the stress values of the intermittent curve are always greater than the stress values of the continuous curve; even when the continuous stress has decayed to zero, there is usually a sizable stress at that time in the intermittent curve. This accords with the observation that in those rubbers whose intermittent curve increases with time, when the stress has decayed to zero in a sample held at constant elongation, the sample is actually found to be very hard, with an extremely large modulus. This might seem rather surprising, since from Equation (14) one would expect that when the stress had decayed to zero, there would be no network chains s left in the rubber, and the rubber sample would be very soft, with no elasticity remaining. An increase or decrease of stress in the intermittent curve corresponds to the hardening or softening which one observes in examining the rubber sample, since the experiment is simply a periodic measurement of the modulus.

Apparently the explanation of these various observations is that, at high temperatures, two reactions occur simultaneously in the rubber: one a scission or breaking of molecular chains, and the other a cross-linking of chains. The two reactions are competing with each other, and the intermittent curve measures the net change in the number of network chains per cc. of the rubber, resulting from the combined effect of both reactions. But apparently the new network chains formed by cross-linking are always formed in relaxed, equilibrium configurations, so their formation does not increase the stress of a sample held at constant elongation. For this reason the continuous relaxation curve is completely unaffected by the cross-linking reaction, measuring only the cutting of those network chains supporting the stress, *i.e.*, those chains originally present in the rubber. Thus the continuous relaxation curve isolates the scission reaction, while the intermittent relaxation curve measures the net effect of both reactions. The intermittent relaxation curve indicates whether scission or cross-linking predominates in the rubber. The intermittent stress values constantly increase in GR-S, which indicates that cross-linking predominates over scission in GR-S from the beginning. The intermittent curve of Butyl decreases rapidly after a period of slight decrease, indicating that scission predominates in Butyl. In Hevea the intermittent curve first decreases, then increases, which indicates that scission predominates initially, but is eventually overtaken by cross-linking. These trends correspond exactly to the observations that GR-S hardens, Butyl softens, and Hevea first softens, then hardens in heat aging.

Continuous and intermittent creep measurements made at high temperatures are also to be interpreted in terms of the scission and cross-linking of the rubber molecules[9]. Intermittent creep measurements are, like intermittent relaxation measurements, simply a periodic measurement of the modulus of the sample, made in an alternate way. Both intermittent creep and intermittent relaxation data give the same curve when they are plotted in an equivalent way, and, of course, measure the same quantity—the net result of cross-linking and scission. The most satisfactory way to plot relaxation and creep data in an equivalent way is to plot s/s_0 as the ordinate for both—the number of chains per cc. of the rubber at time t divided by the number of chains per cc. at zero time. Both types of data can be cast into this form by

use of Equation (14). At zero time we may write that:

$$f_0 = s_0 kT \left\{ \frac{l_0}{l_u} - \left(\frac{l_u}{l_0} \right)^2 \right\} \tag{18}$$

where the zero subscripts indicate zero time. Correspondingly at time t:

$$f = skT \left\{ \frac{l}{l_u} - \left(\frac{l_u}{l} \right)^2 \right\} \tag{19}$$

To obtain s/s_0 we now divide (19) by (18), transpose all but s/s_0 to the other side, and cancel where possible. For stress relaxation, both continuous and intermittent, $l = l_0$ and so we obtain the simple expression:

$$s/s_0 = f/f_0 \tag{20}$$

The significance of s is not the same in the two cases, however. In the intermittent data s signifies the total number of network chains per cc. of rubber at time t; in the continuous data s is the number (per cc.) of those network chains present in the rubber at zero time which still remain uncut at time t. The significance of s_0 is the same for both: The total number of network chains per cc. of the rubber at zero time.

For "creep under constant load", both continuous and intermittent, remembering that $f = f_0$, we obtain from Equations (18) and (19) the expression:

$$s/s_0 = \left\{ \frac{l_0}{l_u} - \left(\frac{l_u}{l_0} \right)^2 \right\} \Big/ \left\{ \frac{l}{l_u} - \left(\frac{l_u}{l} \right)^2 \right\} \tag{21}$$

Here s/s_0 for intermittent creep has the same significance as for intermittent relaxation. In continuous creep, however, a complication enters. If only scission were taking place in the rubber the continuous creep curve would be identical with the continuous relaxation curve (in fact, all four types of curve would be identical). But cross-linking is always taking place at the same time;

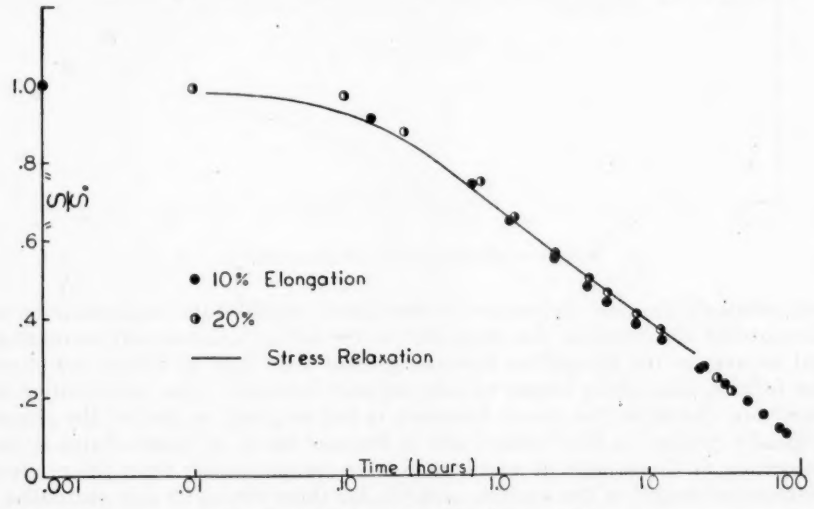


FIG. 16.—Continuous creep; Butyl gum 120° C.

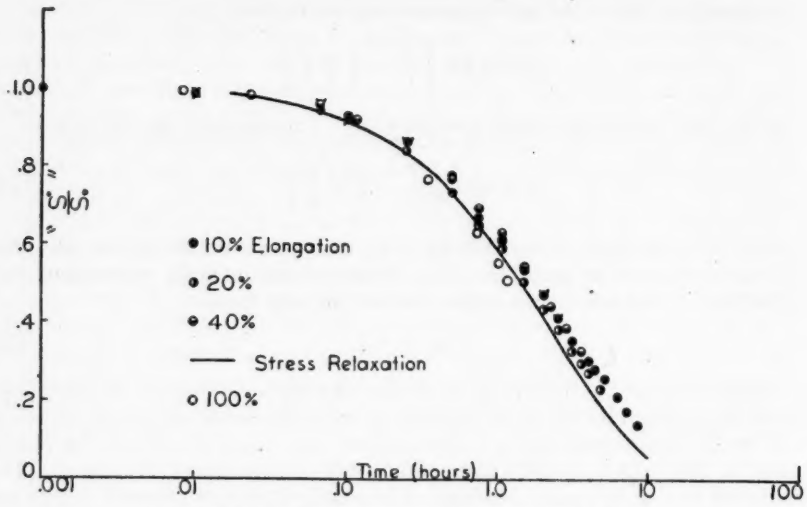


FIG. 17.—Continuous creep; Hevea gum 120° C.

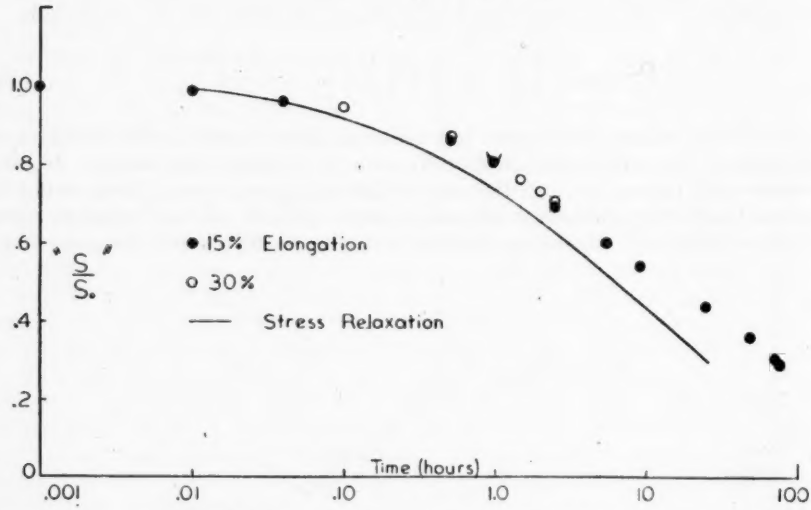


FIG. 18.—Continuous creep; GR-S gum 120° C.

and although the new chains are in unstressed, equilibrium configurations at the moment of formation, the elongation of the rubber is constantly increasing, and as soon as the elongation becomes greater than that at which any chain was formed, that chain begins to help support the load. The contribution of these new chains to the stress, however, is not as great as that of the chains originally present in the rubber; this is because the l_u of these chains is the elongation of the sample at which they were formed rather than the original unstretched length of the sample, and l/l_u for these chains at any particular l is therefore less than the l/l_u for the original chains. Thus the cross-linking

has a retarding effect on the creep rate, and from the considerations given above we would expect the continuous creep curve to be slightly slower than the continuous relaxation curve, the divergence being greatest in those rubbers in which the cross-linking reaction is most marked. This is found experimentally to be the case. Continuous creep data for Butyl, Hevea, and GR-S are shown in Figures 16 to 20. Since the continuous creep curve measures principally scission, but does reflect to some extent the cross-linking going on at the same time, the ordinate is labelled "s/s_0", the quotation marks indicating that the continuous creep values are only pseudo values of the true s/s_0, meas-

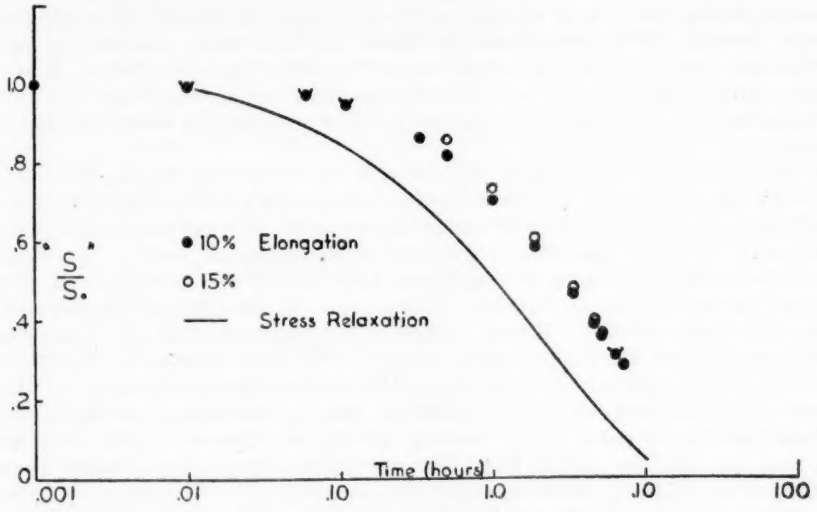


FIG. 19.—Continuous creep; Hevea tread 120° C.

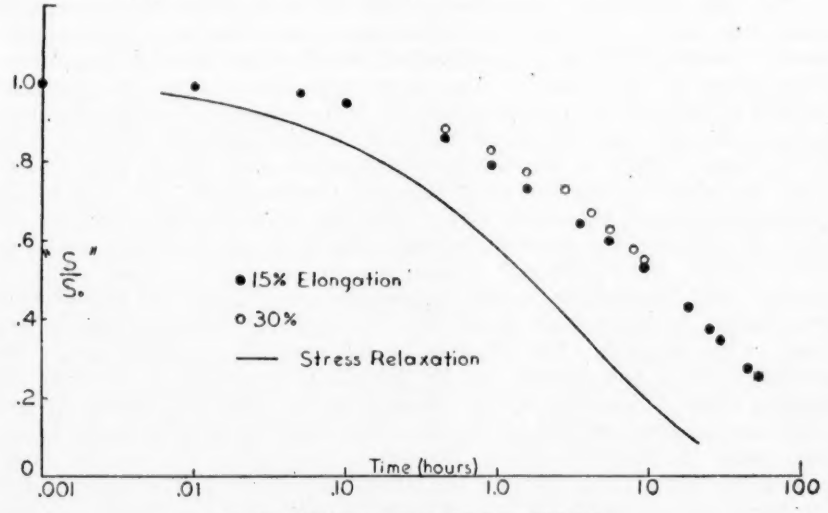


FIG. 20.—Continuous creep; GR-S tread 130° C.

ured by continuous relaxation. The corresponding continuous relaxation curves are shown as solid lines. Continuous creep data at more than one initial elongation are generally shown, incidentally illustrating that the creep curves obtained are identical, within experimental error, from 20 per cent to 100 per cent initial elongation.

It will be seen that no noticeable deviation from the stress relaxation curve is observed in the continuous creep data of Butyl gum at 120° C (Figure 16). The creep data of Hevea gum at 120° C are slightly slower than the relaxation curve (Figure 17), but not to any great extent. In both of these rubbers scission is predominant (in the experimental time the rate of cross-linking has not overtaken the rate of scission in Hevea gum). In Figure 18 continuous creep data at 120° C are shown for GR-S gum, in which cross-linking predominates over scission, and which would, therefore, be expected to show a more marked effect. It is seen that the deviation of the creep data from the relaxation curve is significantly greater in GR-S gum than in Butyl and Hevea gums.

The effect of carbon black can be seen by comparing Hevea tread and GR-S tread (Figures 19 and 20) with the corresponding gum stocks (Figures 17 and 18). It is seen that the deviation is greater in the tread stock than in the gum stock in both cases; this is observed to be the general case. This would seem to indicate that cross-linking occurs more rapidly in the tread stock than in the gum stock, though the rate of the scission reaction has been found to be about the same in both. This is confirmed by a comparison of the continuous and intermittent relaxation curves of gum and tread stocks in Figures 14 and 15. The explanation of this fact is not clear at the present time. It has been suggested that the rubber molecules cling to the surface of the carbon black particles in tread stocks, thereby giving the rubber a higher modulus. It may be that the carbon black particles bring the chain molecules closer together in this way, and thus make cross-linking easier, the effect being the opposite of that of swelling agents, which will be discussed in the following section.

This high-temperature oxidative scission and cross-linking do not manifest themselves only in continuous and intermittent relaxation and creep measurements. Another interesting manifestation is in the dissolution of vulcanizates. When pieces of vulcanizate are heated at fairly high temperatures in a good swelling liquid (such as toluene or xylene), in the presence of small amounts of oxygen, the vulcanizate eventually disintegrates and goes into solution. This is true even of GR-S, in which cross-linking occurs more rapidly than scission when the rubber is heated in air at the same temperatures. The explanation of this phenomenon apparently is that when the solvent swells the rubber, the molecular chains of the network are pushed farther apart, making cross-linking more difficult, while molecular scission remains as easy as before. Thus in swollen GR-S vulcanizate, scission apparently takes place more rapidly than cross-linking, and eventually is effective in completely disintegrating the network of the polymer. The breaking of the network is caused not by the swelling force of the solvent, but by the effect of swelling in changing the relative rates of cross-linking and scission in the polymer. When solvents which are not good swelling agents, *i.e.*, water, acetic anhydride, castor oil, are used under the same conditions, dissolution does not occur, and the cross-linking reaction actually hardens the GR-S vulcanizate[10]. The time required for dissolution is roughly the time required to relax fairly completely in a continuous relaxation test.

The measurement of high temperature cross-linking and scission in raw polymer must be done with special methods. Stress relaxation and creep can of course only be used with vulcanizates. One method of attack is provided by the fact that the molecules of raw polymer can be divided into two groups on the basis of their solubility in a good rubber solvent (benzene or toluene, for example). There is an insoluble or "gel" fraction, consisting of the highly branched molecules and three-dimensional networks; and a soluble or "sol" fraction consisting of the more linear, low molecular weight molecules. Oxidative cross-linking and scission of the molecules cause changes in the character and relative proportions of the sol and gel fractions of the polymer, which can be followed by various methods.

Cross-linking increases the gel fraction and increases the "tightness" (concentration of network junctures per unit volume) of the gel. Scission decreases the gel fraction and makes the gel "looser". When pieces of raw polymer are allowed to stand in benzene or toluene, the sol molecules go into solution, and the gel swells but does not dissolve. By weighing the swollen gel and measuring the concentration of the sol solution, the percentage gel in the polymer can be calculated and also the "swelling index" of the gel (weight of swollen gel, rubber plus absorbed solution, divided by the weight of rubber in the gel), which should give a measure of the "tightness" of the gel. The average molecular weight of the sol molecules can be obtained by measuring the intrinsic viscosity of the sol solution. By making these measurements after various times of aging, the effects of cross-linking and scission can be followed. Evaluating the softening and hardening of the raw polymer by hand test as aging progresses should provide a rough measure of the net effect of cross-linking and scission, much as intermittent relaxation and creep measurements do. The rate of scission can be isolated almost completely by measuring the decrease in intrinsic viscosity of a rubber solution contained in a sealed viscosimeter. The solvent makes cross-linking very difficult by keeping the molecules far apart, while the scission rate is unchanged; the action of the solvent is the same as described in the dissolution of vulcanizates, the effect being even greater here, however.

LOW-TEMPERATURE SECONDARY BOND PHENOMENA

At low temperatures the secondary forces between chains and between portions of the same chain become sufficiently strong, so when the rubber is stretched, many secondary interchain bonds do not relax during the stretching process and thus contribute to the measured initial stiffness of the rubber. These bonds gradually relax, however, and reform in new positions which relieve the stress, so if the rubber is maintained at constant elongation the stress gradually decays until it approaches the equilibrium stress for that temperature as determined by the primary network (see Figure 5).

Intermittent measurements of the stress required to attain a given elongation at low temperatures gives a constant value, provided that the rate of stretching is constant and that the rubber is undergoing no slow crystallization.

The effect of elongation on low temperature stress relaxation is shown in Figure 21, where data for GR-S gum at $-50°$ C are shown for four different elongations: 10 per cent, 20 per cent, 50 per cent, and 100 per cent[11]. Percentage of 10-hour stress is plotted as the ordinate to make the data readily comparable. It appears that in this range of elongations the relaxation curve obtained is independent of the elongation. For the very short time measure-

ments, the 10 per cent data are slightly above the others, but, during the course of the curves as a whole, no regular variation with elongation is found.

The relaxation of stress in rubbers maintained at constant elongation at low temperatures does not follow the Maxwell decay law:

$$f = f_0 e^{-t/\tau} \tag{21}$$

where f is stress, t time, f_0 stress at time $t = 0$, and τ relaxation time. Equation (21) is obtained by integrating Maxwell's equation (1) when $ds/dt = 0$.

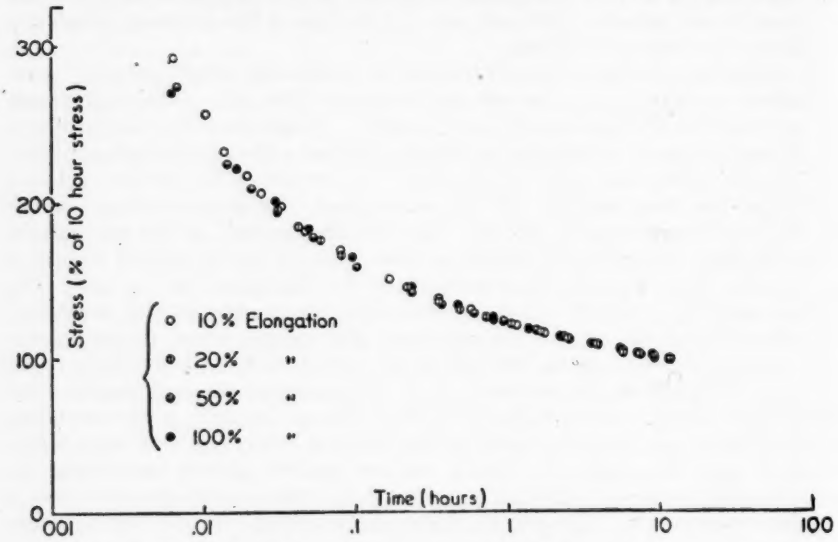


FIG. 21.—Effect of elongation on low-temperature stress relaxation, GR-S gum: −50° C.

The Wiechert generalization of Maxwell's decay law gives:

$$f = \sum_i (f_i)_0 \exp(-t/\tau_i) \tag{22}$$

where we assume a number of relaxation times or in the limit, a distribution of relaxation times. This mathematical result corresponds to a distribution of bond strengths, the relaxation behavior of each type of bond being governed by a linear relaxation law of the Maxwell type. For this case $(f_i)_0$ is the contribution of the ith type of bond to the stress at zero time and τ_i is the relaxation time for the ith type of bond. Equation (22) has the advantage of explaining naturally the fact that the stress decay curves for different elongations differ only by a scale factor (for elongations up to at least 100 per cent) as discussed in the previous paragraph. This theory cannot be considered complete unless the actual distribution in relaxation times can be obtained from first principles. So far as agreement with experiment is concerned, any data can be fitted by a sufficiently complicated distribution of relaxation times.

Other possible relaxation laws exist, in particular the generalized Maxwell equation:

$$\frac{ds}{dt} = \frac{1}{G}\frac{df}{dt} + n\lambda \frac{kT}{h} e^{-\Delta F \mp /RT} 2 \sinh \frac{f\lambda}{2NkT} \tag{23}$$

This equation is nonlinear and the various quantities appearing in it have been defined previously. It may be written in the simplified form:

$$\frac{ds}{dt} = \frac{1}{G}\frac{df}{dt} + A \sinh Bf \tag{24}$$

where

$$A = 2n\lambda \frac{kT}{h} e^{-\Delta F^{\ddagger}/kT}$$

and

$$B = \frac{\lambda}{2NkT}$$

Integrating Equation (24) for the case that $ds/dt = 0$ the following expression is obtained:

$$\tanh\left(\frac{Bf}{2}\right) = \tanh\left(\frac{Bf_0}{2}\right) e^{-k't} \tag{25}$$

where $k' = ABG$.

A graph of the hyperbolic tangent decay function is shown in Figure 22, where f/f_0 is plotted against the logarithm of $k't$. The solid curves are the

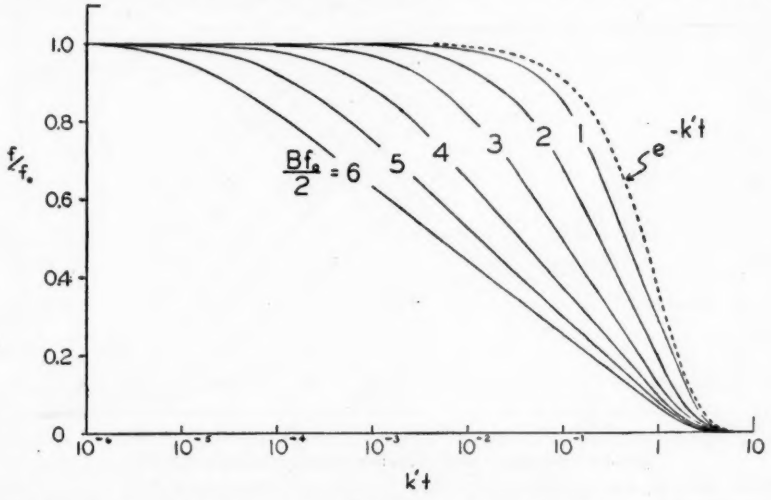


FIG. 22.—Secondary bond relaxation (hyperbolic tangent decay).

decay function for different values of $(Bf_0/2)$, and the dotted curve, included for comparison, is that of the simple first-order decay function:

$$f = f_0 e^{-k't} \tag{26}$$

To explain by this theory the experimental fact that relaxation curves at different elongations differ only by a scale factor, it is necessary that $(Bf_0/2)$ be equal to a constant. Any reason why this should be is not known at present.

As a final example of a decay law that we may derive from *a priori* reasoning let us consider the dissipation of "nonequilibrium" energy. For constant extension experiments we shall assume that the stress and the extra stress

energy (beyond the equilibrium value determined by the primary network) are both functions of the number of secondary bonds that are holding in non-relaxed positions. In the unstretched state the interchain bonds form and reform in new relaxed positions without preference for either position. In the stretched state, however, the "extra" energy causes an asymmetry in the potential curve—in other words, there will be a net tendency for the bonds to move from stressed to relaxed positions with a concomitant dissipation of the excess stress energy. The equation derived from this picture is:

$$-\frac{1}{E}\frac{dE}{dt} = k'\left[e^{\alpha E/kT} - e^{-(1-\alpha)E/kT}\right] \qquad (27)$$

where k' is the specific rate constant associated with the forming and reforming of secondary interchain bonds in the unstretched state, and α is equal to $\frac{1}{2}$ for symmetrical barriers. The integrated form of Equation (27) (exponential integral decay) obtained by neglecting the second term in the bracket on the right-hand side is shown in Figure 23. The stress is presumed to be related to

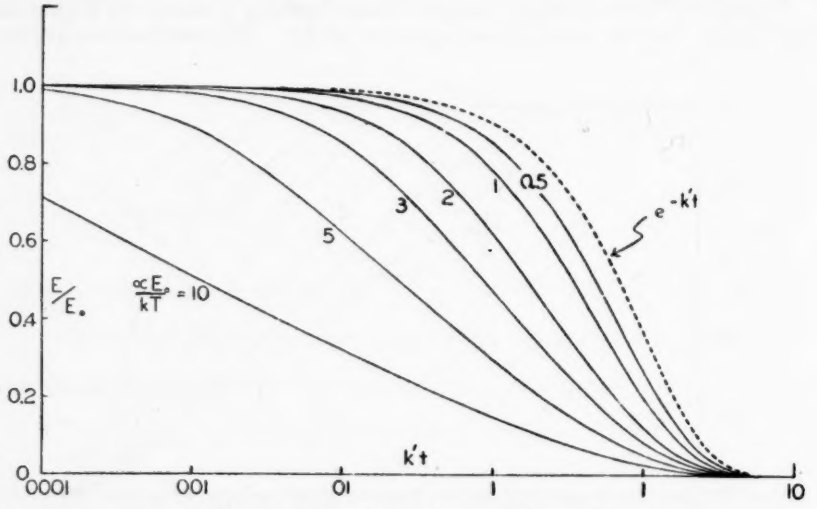


FIG. 23.—Secondary bond relaxation (exponential integral decay).

the energy by some factor of proportionality inasmuch as the material is held at constant extension.

It is apparent that sufficient experimental work is not yet available to make a complete test of any of the theories presented here or elsewhere, although some interesting work has been done in this direction[12]. One of the difficulties is that, at any given temperature, measurements extending over very many cycles of logarithmic time must be made to obtain a complete picture of the stress decay process.

COMPOSITE RELAXATION OF STRESS CURVES

To overcome the difficulty of obtaining experimental results over very extended times, it was observed that relaxation data (plotted in the form of "g" *versus* log t) obtained at one temperature could be superposed on data

obtained at another temperature merely by a translation along the log time axis. The reason for this is obvious in the case of the decay law:

$$\text{“g”} = \text{“g”}_0 e^{-k't} \tag{28}$$

which is obeyed by Hevea gum at high temperatures. The fact that the low-temperature data can also be superposed in this way indicates that the time-temperature dependence of g follows a law of the kind:

$$-dg/dt = \phi(T)\psi(g) \tag{29}$$

How well low-temperature data at different temperatures, either stress relaxation or modulus (measured by the bending creep method of Liska), can be superposed by translation along the log time axis is shown in Figure 24.

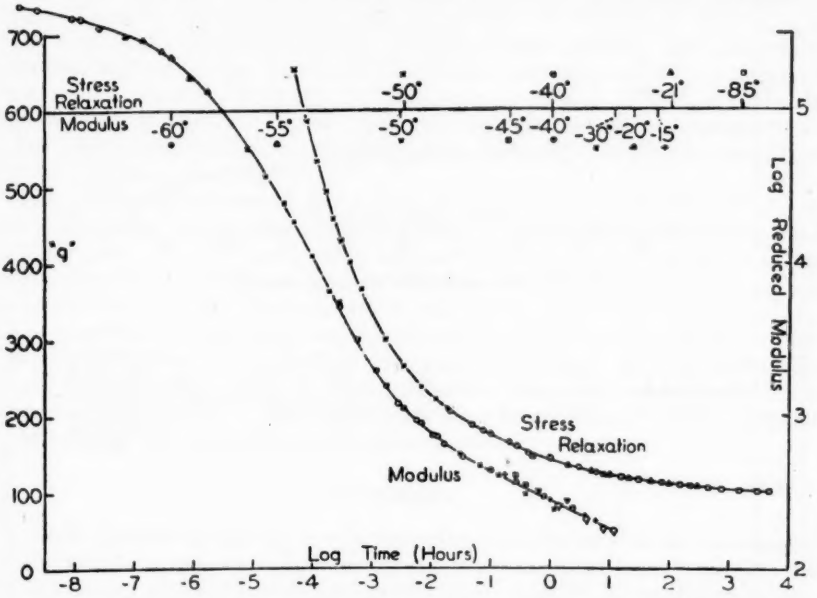


FIG. 24.—Composite stress relaxation and composite low-temperature modulus (GR-S gum).

Values of “g” and the logarithm of the reduced modulus are shown plotted against the log-time scale appropriate for −40° C. The origin of the log-time scale for each temperature is shown in the scale on top of the page. The one-hour value (log time equals zero) is marked for each temperature on this scale, and the log-time scale below can be used for each temperature merely by reference to the correct origin. The different types of points represent data at different temperatures.

By this method a single graph can be used to show the complete stress-temperature-time relations of a rubberlike substance. Figures 25 and 26 based on the same principle as Figure 24 are complete “stress biographies” of the Hevea and GR-S gum and tread stocks studied. From these figures the complete stress-time-temperature behavior of these rubbers can be determined for times that would be impossible to attain experimentally. Even though “g”, the reduced stress, is plotted only as 50 per cent elongation data, the curves

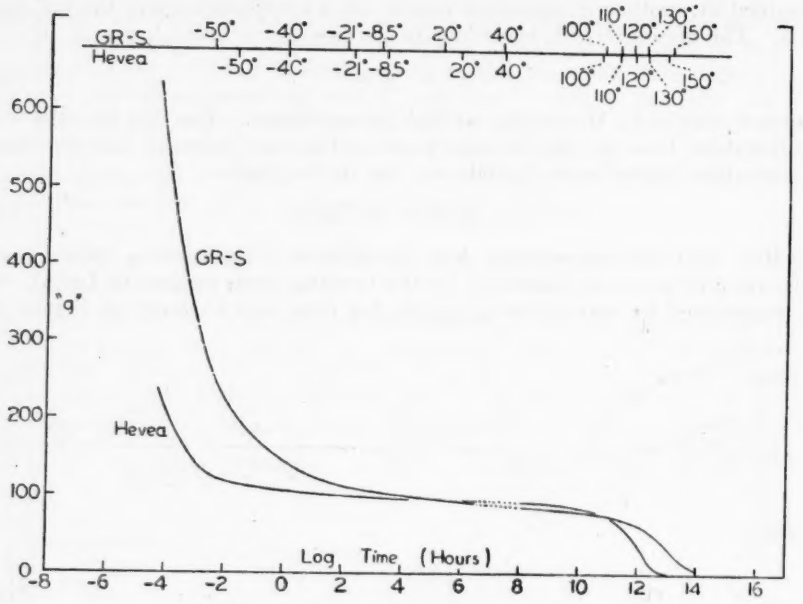


FIG. 25.—Composite stress relaxation gum stocks.

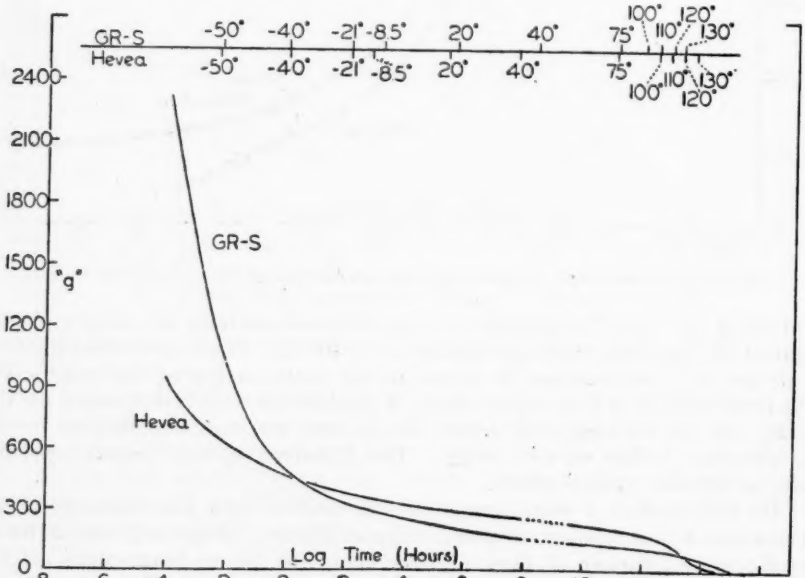


FIG. 26.—Composite stress relaxation tread stocks.

have greater generality, because at different elongations these curves would be altered only by a scale factor in the ordinate.

It should be remembered that two processes are shown in these composite curves, primary and secondary bond relaxation, with very different activation energies, and therefore different temperature coefficients. For this reason it is to be expected that if the primary bond relaxation at two different temperatures is superposed, the secondary bond relaxation at the two temperatures will not be superposed in that position. Two composite curves are really needed, one for primary and the other for secondary bonds, with the time origin for each temperature marked on the log time abscissa of each. Then to obtain the complete relaxation curve at any temperature, one would slide the first graph along the second until the two log time origins for that temperature coincided. Dotted lines are used to connect the primary and secondary regions of the composite curves in Figures 25 and 26 to indicate this—that a single continuous relaxation curve, including both primary and secondary relaxation regions, is not universal for all temperatures, simply by choosing the appropriate point along the log time scale as origin. The reason that a single curve was obtained in the graphs shown here was merely the result of the fact that, in most of the superposition, one or the other of the two relaxation regions was being superposed.

The conclusions stated in this section of course depend on the validity of the superposition procedure. It seems fairly clear at the present time that the superposition procedure is truly applicable at high temperatures, *i.e.*, for the primary bond relaxation region. The position of the origin on the log time scale for any temperature can be calculated by use of Equation (17). At low temperatures the data used overlapped only to a small extent, so that it was very difficult to tell whether the curves at different temperatures really would superpose completely. Low-temperature data over more extended times are needed to check this. For this reason the conclusions expressed here must be regarded as only tentative at the present time.

SUMMARY

Actual substances exhibit a very complicated behavior under mechanical stresses which cannot be described by classical elasticity theory nor by the classical theory of the hydrodynamics of viscous fluids. A general molecular theory describing the behavior of matter under stress is discussed and related to previous investigations and to experimental observations. Particular attention is devoted to rubberlike substances for which the classical theories are definitely inadequate. Experimental results on relaxation and creep of rubbers are interpreted in terms of modern structural concepts. It is found that these substances exhibit three regions of stress-temperature-time dependence. At intermediate temperatures there is a region of relative stability in which the statistical-thermodynamic theory of rubber elasticity is valid. At elevated temperatures, relaxation and creep are caused by chemical changes involving the rupture and formation of primary valence bonds. These chemical changes, which are responsible for the aging of rubber, can be isolated and studied by appropriate experimental techniques. At low temperatures relaxation and creep are caused by the slipping of secondary interchain bonds which are breaking and reforming in times comparable to experimental times of measurement. Theories are advanced to explain the observed stress-temperature-time behavior of rubbers over the entire temperature range studied.

ACKNOWLEDGMENTS

The authors wish to thank the Firestone Tire and Rubber Company and Princeton University for making possible our researches on fundamental physical properties of rubber. In particular we wish to thank H. S. Taylor of Princeton University, and J. N. Street, J. H. Dillon and I. B. Prettyman of Firestone for the coöperation, encouragement, and useful advice they have tendered us.

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[3] Tobolsky and Eyring, *J. Chem. Phys.* **11**, 125 (1943).
[4] Wall, *J. Chem. Phys.* **10**, 485 (1942); Guth and James, *J. Chem. Physics* **11**, 455 (1943).
[5] Tobolsky, Prettyman and Dillon, *J. Applied Physics* **15**, 380 (1944).
[6] The data quoted here on relaxation of stress at constant extension are in general taken from Reference 5, where complete details as to experimental procedure are given. In a few cases data which were obtained in connection with the experimental work on Reference 5, but not published then, are given here for completeness.
[7] Liska, *Ind. Eng. Chem.* **36**, 40 (1944).
[8] These data were kindly supplied by J. W. Liska of the Firestone Physics Research Division, and have been more fully discussed by him at the June 1944 meeting of the Division of High-Polymer Physics. We wish to thank Dr. Liska for extending this courtesy.
[9] Mesrobian, Andrews and Tobolsky, incorporated in Senior Thesis of R. B. Mesrobian, Princeton University, **1944**.
[10] Unpublished experiments by M. Magat and A. V. Tobolsky.
[11] These data were sent to us through the courtesy of I. B. Prettyman of the Firestone Physics Research Division.
[12] Mooney, Wolstenholme and Villars, *J. Applied Physics* **15**, 324 (1944).

COMPARISON OF THE STRUCTURES OF STRETCHED LINEAR POLYMERS *

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x-Ray diffraction data show that substances composed of long chain molecules, when stretched, if not otherwise, tend to form crystalline arrangements in which the chain axes lie parallel to each other. In some cases, as in polyethylene[1], polyvinyl alcohol[2], and polyvinyl chloride[3], the data indicate a planar zigzag arrangement of the chain atoms in each chain (Figures 1 and 2).

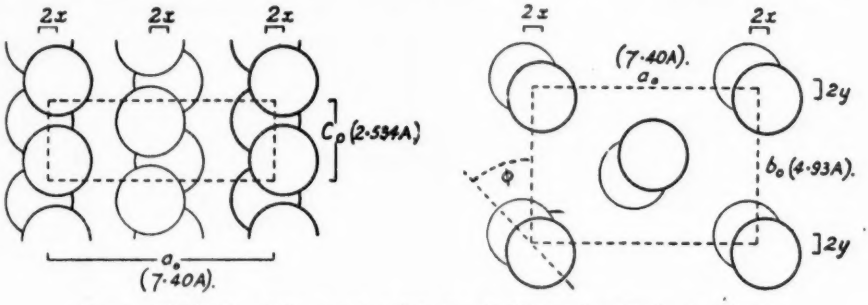


FIG. 1.—Distribution of zigzag carbon chains in polyethylene, $(-CH_2-)_n$, according to Bunn (reference 1).

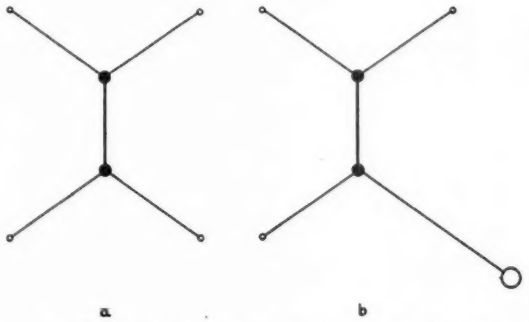


FIG. 2.—Projections of proposed structures for polyethylene (a) and polyvinyl alcohol (b). The hydroxyl hydrogen atoms of the latter are not shown. Polyvinyl chloride is presumed to have a structure like (b), but with the Cl atoms of the CHCl groups alternating from one side to the other of the plane of the C—C zigzag.

Each chain is extended as far as possible, consistent with maintenance of the expected bond distances (~1.53A for C—C) and bond angles (~110° for ∠C—C—C). In most instances, however, the data are not in agreement with such a structure. The number of chain atoms between like points in a

* Reprinted from *The Journal of Chemical Physics*, Vol. 13, No. 1, pages 37–42, January 1945. This paper was presented at the Inaugural Meeting of the Division of High-Polymer Physics, Rochester, N. Y., June 24, 1944.

TABLE I

DATA FOR VARIOUS POLYMER STRUCTURES

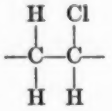
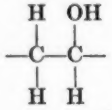
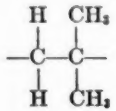
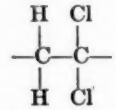
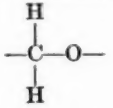
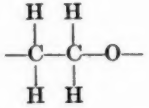
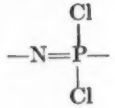
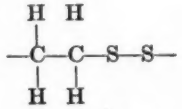
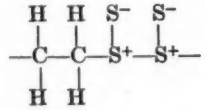
Polymer	Repeating unit	Identity distance (t)	Bond distance (assumed)	Bond angle (calc.)	No. of chain atoms per identity distance (m)	No. of revolutions per identity distance (p)	Rotation per chain bond (α)	
Polyethylene	$-CH_2-$	2.534A	1.53A	112°	2	1	180°	
Selenium	—Se—	4.95	2.32	105°	3	1	120°	
Tellurium	—Te—	5.91	2.86	102°	3	1	120°	
Sulfur	—S—	9.26	2.12	107° 107°	8 6	2 2	90° 120°	Reverse ? Reverse ?
Polyvinyl chloride		5.0	1.53	110°	4	2	180°	
Polyvinyl alcohol		2.52	1.53	110°	2	1	180°	
Polyisobutylene		18.63	1.53	111°	16	7	157.5°	
Polyvinylidene chloride		4.67	1.53	122°	4		Not a uniform spiral	

TABLE I—*Continued*

Polymer	Repeating unit	Identity distance (t)	Bond distance (assumed)	Bond angle (calc.)	No. of chain atoms per identity distance (m)	No. of revolutions per identity distance (p)	Rotation per chain bond (α)		
Polyoxymethylene		17.3	1.43	111°	18	5	100°		
Polyoxyethylene		19.5	C—C 1.53 C—O 1.43	108° 110° (assumed)	24 27	6 5	90° non-uniform spiral	Reverse	? ?
Polyphosphonitrile chloride		4.92	1.65	124°	4	1	90°		
Polyethylene disulfide		8.8	1.825 (Av.)	111°	8	2	90° (Av.)	Reverse	?
Polyethylene tetrasulfide		4.32	1.825 (Av.)	110°	4	1	90° (Av.)		

chain is greater than two and the "identity distance"—the distance between consecutive like points—differs from what would be expected for a plane zigzag arrangement. In this paper, the structures of these substances are discussed.

In accordance with well established principles of structural chemistry, we should expect a chain composed of chain atoms which are equivalent as regards the atoms to which they are bonded to assume a structure (on crystallization) in which these chain atoms are in crystallographically equivalent positions. This requirement is satisfied by a planar zigzag structure or by a unidirectional spiral structure of uniform pitch. Which type is assumed in a given case (and the constants of the spiral, if the latter) will depend on intra- and inter-chain forces, as discussed below.

Polyethylene[1] $(-CH_2-)_n$, and crystalline "metallic" selenium[4] and tellurium[4] are composed of chain molecules in which the chain atoms (C, Se, Te)

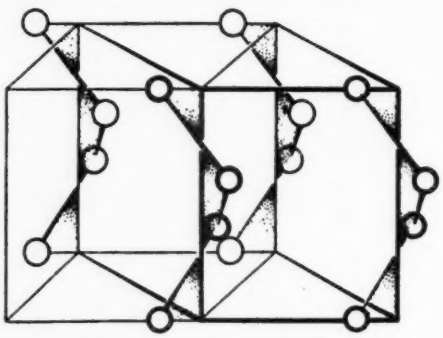


FIG. 3.—The structure of Se and Te crystals.[5]

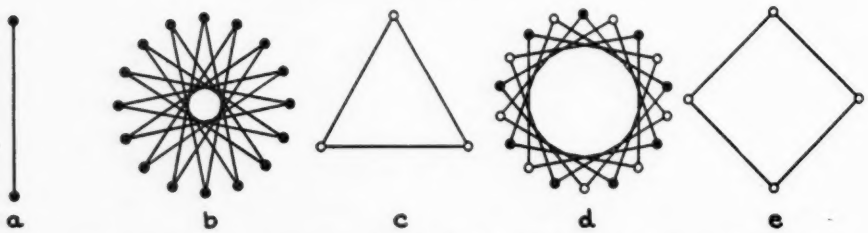


FIG. 4.—Projections of the chain atoms and bonds in certain structures, assuming uniform spirals. (a) Polyethylene, polyvinyl alcohol, polyvinyl chloride. (b) Polyisobutylene. (c) Selenium, tellurium. (d) Polyoxymethylene. (e) Polyphosphonitrile chloride, polyethylene tetrasulfide.

are all equivalent. In polyethylene, the chains have the planar zigzag structure; in selenium and tellurium, the chains are uniform spirals with three chain atoms per identity distance (Figures 3[5] and 4). The bond distances and bond angles (Table I) agree with what would be expected from structure theory and from our knowledge of corresponding distances and angles in the substances.

A planar zigzag structure can be considered as a special case of a uniform spiral, in which for each bond in the chain there is an angular rotation (α) of $360°/2$ and a translation of $t/2$, where t is the identity distance. In selenium or tellurium, the angular rotation and translation per chain bond are $360°/3$ and $t/3$, respectively. In general, for a uniform spiral, there is, per chain

bond, an angular and translational shift of magnitudes $p360°/m$ and t/m, respectively, where p and m are integers. From x-ray data, t and m may be deduced. Knowing these, one can compute a value of α corresponding to any pair of assumed values of bond distance and angle. If p, computed from the equation:

$$p = \alpha m/360°$$

is found to be approximately integral, values of bond distance and angle close to those assumed are consistent with the assumption of a uniform spiral and with the experimental t and m values. By assuming p to be exactly integral, one can then compute the exact value of bond angle consistent with the observed t and m values and an assumed bond distance. This procedure was followed in deducing the bond angles in Table I. (Alternatively, one might assume bond angles and deduce bond distances.)

The data on fibrous sulfur should be mentioned. Meyer and Go[6] have deduced unit-cell dimensions, including a fiber period of 9.26A, and suggested (on the basis of very meager evidence) that there are 14 chains of 8 S atoms, each passing through this cell. Meyer later proposed, as an alternative, 16 chains of 8 atoms each. The published data seem to be in as good or better agreement with 18 chains of 6 atoms each. Either 8 or 6 atoms per 9.26A in the fiber direction would be consistent with the assumption of uniform spirals if one permits two complete rotations per identity distance (see Table I). The doubled identity distance could be accounted for by assuming a reversal of direction of the helix after each complete rotation (Figure 5). Obviously, a more detailed structure analysis is required.

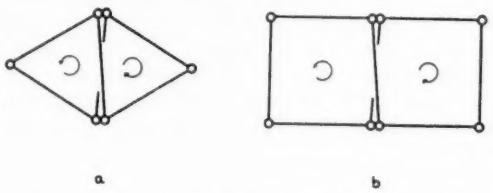


FIG. 5.—Projections of two possible reverse spiral structures for fibrous sulfur. So as to show better the spiral arrangements, the projections of the middle atoms, in both structures, have been shifted slightly from their true positions. A structure of the type of (b) may also be correct for polyoxyethylene and polyethylene disulfide.

Plane zigzags or uniform spirals are also necessary when alternate chain atoms are different with respect to their attachment to other atoms, as in vinyl polymers, if all the bonds in a chain are equivalent. Interaction between the groups attached to the chain atoms within each chain or between neighboring chains may, however, make another arrangement more stable. (See the discussion of polyvinylidene chloride below.)

Polyvinyl chloride[3] and polyvinyl alcohol[2] give x-ray data which agree with a plane zigzag structure having the customary C—C distances and ∠C—C—C bond angles. The identity distance in polyvinyl chloride is approximately twice that in polyvinyl alcohol. As pointed out by Fuller, the larger value would be expected if the chloride atoms are alternately placed, first on one side and then on the other, with respect to the plane of the zigzag (Figure 2).

x-Ray data from polyisobutylene have been interpreted by Fuller, Frosch, and Pape[7] as showing 16 chain atoms per fiber period, 18.63 ± 0.05A. These

figures are in agreement with the assumption of a uniform spiral with tetrahedral bond angles and the usual C—C distance. The angular shift α is 157.5°. The departure from a plane zigzag structure, for which $\alpha = 180°$, is thus not very great (Figures 4 and 6).

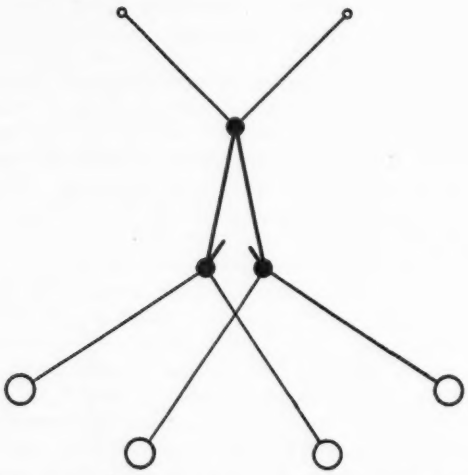


FIG. 6.—Projection of a small section of a polyisobutylene spiral. Large circles denote carbon atoms of methyl (CH_3) groups.

Reinhardt[8] has reported a fiber period of 4.67A for polyvinylidene chloride with 4 chain atoms (two residues) per unit in each chain. These data are not in accord with a uniform spiral structure. The arrangement (Figure 7) he proposes is a reasonable one, although it is necessary to assume a C—C—C bond angle greater than 120°. The type of arrangement can be attributed to strong interaction between the side atoms, H and Cl, of opposite polarity.

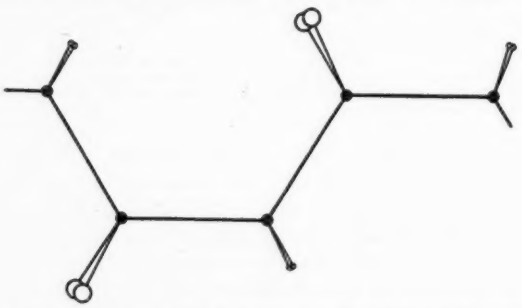


FIG. 7.—Projection of the polyvinylidene chloride structure onto the plane of the —C—C— chain, according to Reinhardt. The positions of the H and Cl projections have been displaced slightly.

In polyoxymethylene, $(—CH_2—O—)_n$, as in the vinyl polymers, the chain atoms are alternately of two types: Both OCO and COC bond angles would be expected to be in the neighborhood of "the tetrahedral angle". The C—O distance should be about 1.43A. These expectations and the experimental value[9] of the fiber period, 17.3A for 9 $—CH_2O—$ groups (18 chain atoms), agree with the assumption of a uniform spiral (Table I and Figure 4).

In polyoxyethylene or polyethylene oxide $(—CH_2—CH_2—O—)_n$, the chain bonds are not all alike. The assumption of a uniform spiral, with the expected bond distances and with all bond angles in the neighborhood of 110°, leads to an identity distance just one-third of the experimental value[10]. There is no obvious reason for this discrepancy. It is likely that in this case the assumption of a spiral of uniform slope is in error. There is no symmetry argument for it, and it is certainly reasonable to expect better packing and greater

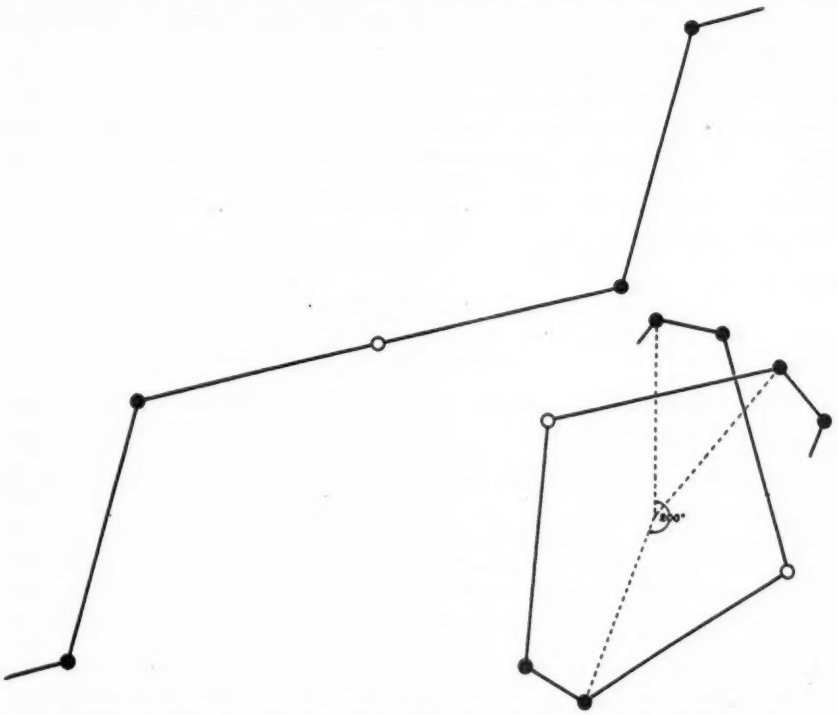


FIG. 8.—Illustrating a possible structure for polyoxyethylene (polyethylene oxide), $(—CH_2—CH_2—O—)_n$. A projection of a portion of the helical chain is shown at the lower right. Above and to the left is the arrangement obtained by unrolling the helix onto a plane; this shows the different pitch of the C—C and C—O—C portions of the chain.

stability for a structure in which the slope of the C—C bonds differs from that of the C—O and O—C bonds. Assuming a unidirectional spiral with slopes of C—O and O—C bonds the same and with 110° bond angles throughout, the observed identity distance[11] is found to correspond to 5 revolutions of the chain, with the C—C bonds nearly parallel to the spiral axis (the projection of the 1.53A bond distance on the axis is 1.48A) (see Figure 8). This differs considerably from the meandering structure assumed by Sauter[12], in which the C—C bonds are roughly perpendicular to the chain axis.

Sauter's conclusion that there are 9 $—CH_2—CH_2—O—$ residues per identity distance, in the polyoxyethylene structure, is questionable[13]. If there should really be only 8 such residues per identity distance, a reverse spiral of uniform slope would be possible. [See Table I and Figure 6(b).] Further structure work is obviously necessary.

Polyphosphonitrile chloride is another substance which consists of chain molecules in which the chain atoms are alternately of two types. The structure can be considered as resonating, according to the scheme:

$$\left[\begin{array}{c} Cl \\ -N{=}P- \\ Cl \end{array}\right]_n \leftrightarrow \left[\begin{array}{c} Cl \\ {=}N{-}P{=} \\ Cl \end{array}\right]_n$$

The distance between adjacent N and P atoms can be taken as 1.65A, the value found by Brockway and Bright[14] for the trimer, a ring compound, by electron diffraction methods.

Meyer, Lotmer, and Pankow[15], in their x-ray study of the polymer, deduced 4.92 ± 0.05A for the fiber period, and concluded that there are 4 chain atoms in this distance. From these results, the assumption of a uniform spiral leads to an average bond angle, $\angle$PNP or $\angle$NPN, of 124° (Table I and Figure 4). This is reasonable, being close to 125° 16′, the calculated angle between a single and a double bond for regular tetrahedra. In the trimer ring, the average angle is about 120°.

In polyethylene disulfide, $(-CH_2-CH_2-S-S-)_n$, and polyethylene tetrasulfide:

$$\left[\begin{array}{c} \quad\quad S\ \ S \\ \quad\quad \| \quad \| \\ -CH_2-CH_2-S-S- \end{array}\right]_n$$

as in polyoxyethylene, symmetry and similar arguments do not require uniform slopes for the chain bonds. Nevertheless, the observed fiber distances[16] agree with the assumption of spirals of uniform pitch with approximately tetrahedral bond angles (see Table I and Figures 4 and 5)—a reverse spiral in the case of the disulfide.

With regard to rubber, gutta-percha, polychloroprene, polyamides, polyesters, and other substances composed of chains more complex than those already considered, we might expect uniform, or nearly uniform, spirals except when prevented by strong atomic interactions (other than those determining the bond distances and angles), either within the same chain or between chains. Detailed consideration of these structures will not be attempted at this time.

The angular shift per chain atom in a molecular spiral may be determined primarily by the requirements for most stable (lowest energy) packing of the chain molecules in the mass or by forces between atoms in the same chain. In addition, if the substance is held under tension, there is the stretching force tending to extend the chain in the direction of its axis as much as possible. If not prevented by other forces, this stretching force produces a plane zigzag arrangement—the most extended one possible for given bond angles and distances. Intrachain forces may make this structure impossible, as, for instance, in the case of polyisobutylene, in which repulsion between the methyl groups on alternate carbon atoms forces a small angular shift of these atoms around the chain axis (Figure 6). In a case such as selenium or tellurium, the form of spiral is probably largely determined by forces between atoms in different chains, tending to produce an arrangement of atoms as closely packed as possible consistent with the maintenance of stable bond distances and angles.

In conclusion, it must be emphasized that most of the structural arrangements which have been discussed require further experimental confirmation. Work along this line is planned by the writer when war conditions permit. Meantime it must be considered interesting and probably significant that, of

the variety of simple polymer structures for which identity distance data are available, nearly all are in accord with the simple reasonable hypothesis of uniform spiraling.

SUMMARY

Published x-ray data from crystalline selenium and tellurium and from stretched sulfur (amorphous), polyethylene, polyisobutylene, polyvinyl alcohol, polyvinyl chloride, polyvinylidene chloride, polyoxymethylene, polyoxyethylene, polyethylene disulfide, polyethylene tetrasulfide, and polyphosphonitrile chloride are compared. In most cases the experimental identity-distance in the direction of the chain axes and the expected interatomic distances and interbond angles are found to be in agreement with the assumption that the chain atoms form a regular spiral, unidirectional in each chain and of uniform pitch. Apparent exceptions are briefly discussed.

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A THEORY OF THE CALENDER EFFECT IN RUBBERLIKE MATERIALS *

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When raw rubber and many rubberlike materials are calendered, an anisotropy is produced. This effect—the calender effect—is well known[1], and is due to some sort of "freezing in" of the strains produced during calendering. The presence of these strains and the stresses to which they give rise can be shown by the anisotropy in mechanical properties and more strikingly by the effects of warming. The behavior associated with the calender effect may be conveniently summarized under two headings.

1. *Residual Strain.*—If a sheet of calendered material (exhibiting the calender effect) is warmed, it will contract, if free to do so, in the direction of calendering and expand in the remaining two directions. This may be said to be due to the presence of residual strains in the calendered sheet. The socalled residual strain is positive, *i.e.*, a tensile strain, in the direction of calendering and negative, *i.e.*, a compressive strain, in the remaining two directions. The presence of these strains may also be shown by the smaller percentage elongation at break in the direction of calendering than in a direction perpendicular thereto.

2. *Residual Stress.*—If the calendered sheet is held so that it is not free to contract in the direction of calendering, when warmed a tension will be set up in this direction and an external stress will have to be exerted to prevent the contraction of the sheet. This may be said to be due to the presence of residual stresses in the calendered sheet. The socalled residual stresses will be in the same directions as the corresponding residual strains, and their presence may also be shown by the lower tensile strength in the direction of calendering than in a direction perpendicular thereto.

SOME EXPERIMENTAL DATA

Some experiments carried out with calendered P.V.C. (plasticized polyvinyl chloride) illustrate the calender effect.

(1) Strips 2.5 cm. wide, 18 cm. long and 0.1 cm. thick were cut with their length in the direction of calendering. A strip was immersed so as to hang freely in a bath of glycerine, maintained at a constant temperature, for ten minutes and then immersed in water at room temperature for 5 minutes. The percentage retraction was measured on 15 cm. of the strip. This experiment was carried out at a series of temperatures from 20° to 180° C, a fresh strip being used for each test. A typical curve is shown in Figure 1.

(2) Similar strips were placed in two brass clamps 15 cm. apart (see Figure 2). The lower clamp was fixed, while the upper one was attached to a brass strip. A cord from this strip passed over a pulley wheel to a scale pan. A rod on the brass strip operated a mirror on a pivot. An extension or con-

* Reprinted from the *Transactions of the Faraday Society*, Vol. 41, No. 2, pages 81–87, February 1945.

traction of the strip under test was shown (magnified 200 times) by the movement of a spot of light reflected by the mirror. The strip was surrounded by an electrically heated and thermostatically controlled air bath, the temperature of which—as indicated by a mercury thermometer—could be maintained constant to within about 1° C. The stress required to keep the strip at its original length was measured at a series of temperatures by the weights that had to be

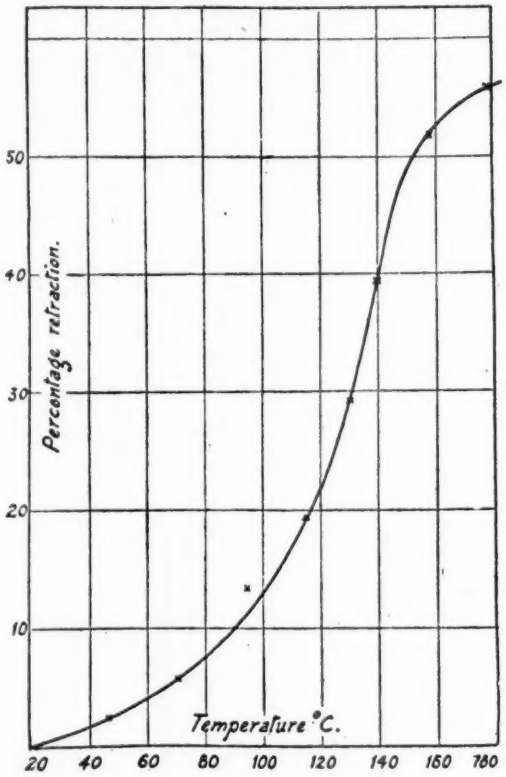

FIG. 1

added to the scale pan in excess of the zero load. These weights were constantly adjusted so that the spot of light remained in the same position. On raising or lowering the temperature, approximately one-half hour was required for the bath to settle down to its new temperature and for the stress to rise or fall to an equilibrium value. (The stress was regarded as at its equilibrium value, provided that it was constant to within 4 grams per sq. cm. over a period of 10 minutes.)

The equilibrium stress was recorded at a series of increasing temperatures from 20° to 120° C, and thereafter at a series of decreasing temperatures. A typical curve is shown in Figure 3. A further heating and cooling cycle gave curves coincident with CDE. No corrections were made for thermal expansions. The figure shows that the stress reaches a maximum value at 80–90° C.

The stress required to hold the strip at constant length is equal and opposite to the retractive stress in the strip, and ignoring the sign will be referred to below as the retractive stress.

DEFORMATION IN RUBBERLIKE MATERIALS

The deformation, D, produced in a rubberlike material by the action of a constant stress S can be analyzed into three components[2].

(1) An ordinary elastic deformation, D_{OE}, proportional to S and appearing and disappearing instantaneously on the application and removal of the stress. For P.V.C.[3] the modulus, $n_1 = S/D_{OE}$, is independent of temperature, and is of the order 10^{10} dynes per sq. cm. This type of deformation corresponds to a stretching of the polymer chains.

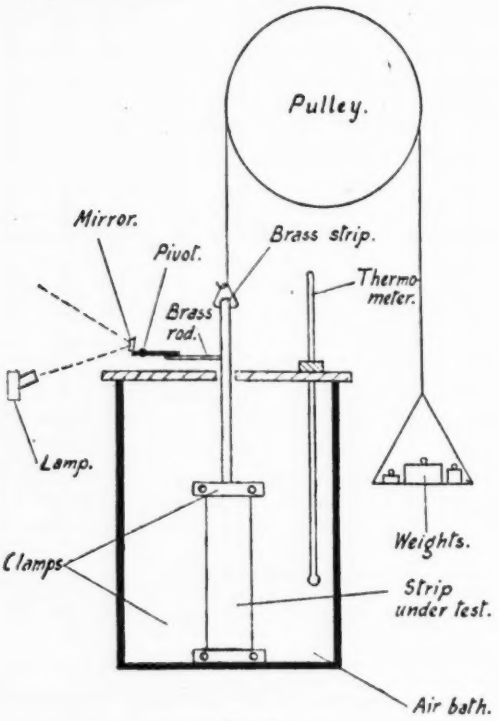

FIG. 2

(2) A high elastic deformation, D_{HE}, proportional to S and requiring a time for its full appearance and disappearance, depending on the temperature. At a temperature of 60–100° C, when for P.V.C. the time for the full development of the deformation is relatively small, the modulus, $n_2 = S/D_{HE}$, is of the order of 10^6 dynes per sq. cm. This type of deformation corresponds to the uncurling of the polymer chains and the temperature dependence of the time effect is connected with the variation with temperature of the viscosity of the plasticizer.

(3) An irreversible "plastic" deformation, $D_{VISC.}$, proportional to S and to the time of application. The "viscosity" coefficient, $\eta_1 = St/D_{VISC.}$, for this

type of deformation falls with temperature and, for P.V.C., is of the order 10^4–10^5 poises at 140° C. This deformation corresponds to the sliding of the polymer chains past each other.

The behavior of such a material can be represented by the well known model system[4] of Figure 4 consisting of elastic elements (springs) and viscous

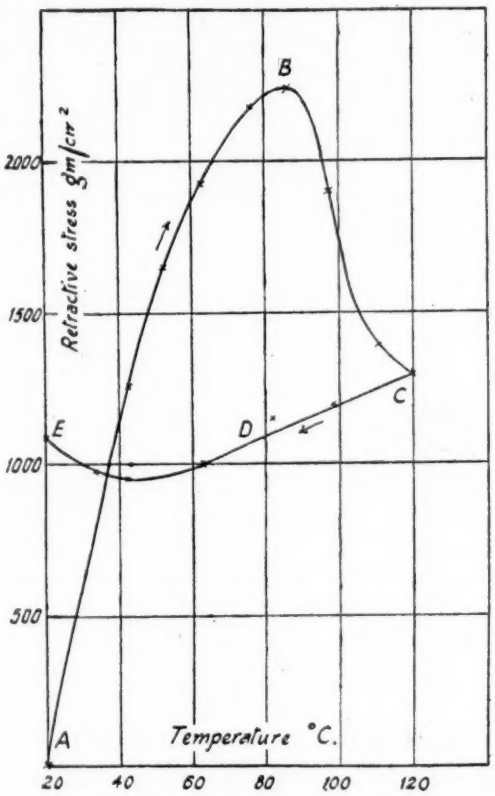

FIG. 3

elements (dashpots) obeying Hooke's and Newton's laws, respectively. It can easily be shown that for such a model:

$$D = D_{OE} + D_{HE} + D_{VISC.} = \frac{S}{n_1} + \frac{S}{n_2}(1 - e^{-(n_2/\eta_2)t}) + \frac{St}{\eta_1} \qquad (1)$$

It is clear that this model, as it stands, is not capable of providing an explanation of the experimental facts described above in connection with the calender effect. For, suppose that the model is stretched at some high temperature and then rapidly cooled in an attempt to simulate calendering conditions. After sufficient time has elapsed all the internal stresses of the model dissipate. Owing to the presence of the viscous elements, the model is not capable of retaining deformations, whereas experiments have shown that in P.V.C. sheets kept for 6 months (at 30° C) no measurable change in the calender effect could

be detected. If, however, we are prepared to associate temperature-dependent yield values, f_1 and f_2, with the viscous elements, η_1 and η_2 it is possible to account for the experimental data described above in terms of the now modified model system of Figure 4.

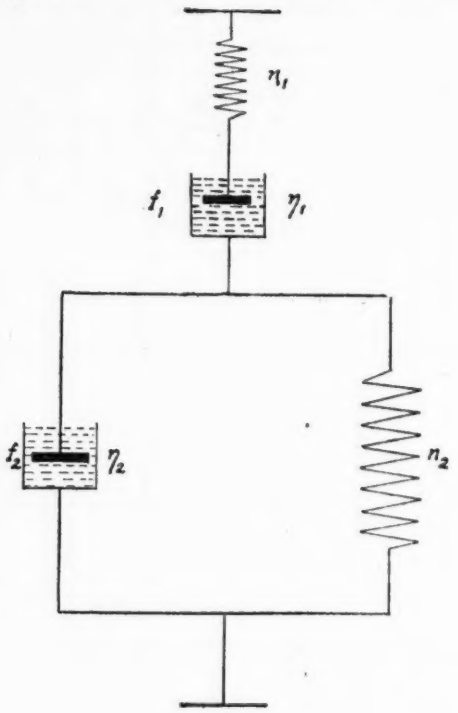

FIG. 4

MODEL FOR THE CALENDER EFFECT

Suppose we attempt, as a preliminary, to represent the behavior of a calendered strip by a model consisting of an elastic element in parallel with a "viscous" element possessing a yield value (see Figure 5). Let n_2 be the modulus of the spring and η_2 and f_2 the "viscosity" coefficient and yield value of the dashpot. If this model is strained to a value of strain x, then the stress R required to hold it at this strain is given by:

$$R = S - f_2$$

where $S = n_2x$ is the stress in the elastic element. Suppose that the model still held at the strain x is now cooled and that the yield value f_2 rises with falling temperature. If the model is now released it will exhibit some recovery only if S is greater than the yield value at this temperature. Had a temperature been chosen such that the yield value was equal to S, the model on release would exhibit no recovery. The retractive stress R would then be zero, the residual stress S being exactly balanced by the yield value of the dashpot. If the temperature is now raised, the stress R required to hold the model at the strain x increases, owing to the decrease of the yield value with increasing

temperature. If $R(\theta)$ represents the dependence of R on temperature θ and $f_2(\theta)$ that of f_2, we can write:

$$R(\theta) = S - f_2(\theta) \tag{2}$$

Equation (2) and the model of Figure 5 does not, however, provide a complete account of the R/temperature curve, since it does not permit of R falling at sufficiently high temperatures. Let us now consider the effect of the second dashpot, viscosity coefficient η_1 and yield value f_1, in series with the parallel model. We repeat the procedure described above. Supposing that f_1 is very much greater than f_2, we see that, on warming, no movement can take place

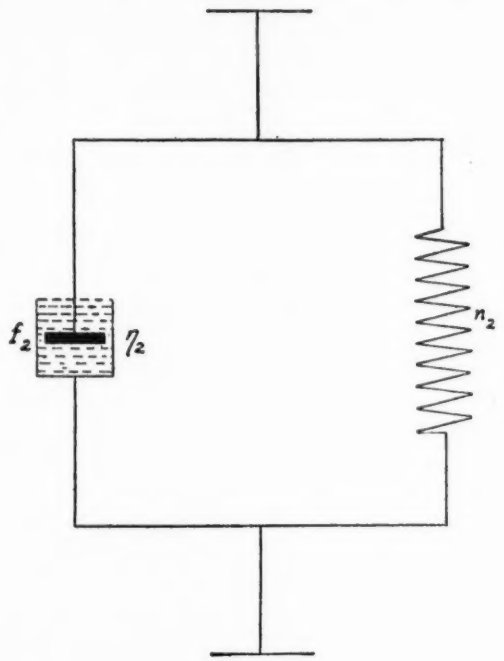

FIG. 5

in η_1 until the temperature is sufficiently high for R to have increased and f_1 to have decreased to make R equal to f_1. A further increase in temperature produces an instantaneous increase in R (owing to a decrease in f_2), whereupon flow takes place in η_1. As this flow continues the strain x in the spring n_2 decreases and R decreases until it is just equal to f_1. The value of R at this and higher temperatures is wholly dependent on the values of f_1 and we can write:

$$R(\theta) = f_1(\theta) \qquad f_1(\theta) + f_2(\theta) \leqslant S$$

S being the original value of the stress in n_2.

The temperature at which $S = f_1(\theta) + f_2(\theta)$ is the temperature at which annealing begins to take place, *i.e.*, the temperature at which the residual stress S begins to be relaxed by the plastic flow that takes place in η_1. The

residual stress S_1 at some higher temperature is given by:

$$S_1(\theta) - f_2(\theta) = f_1(\theta) = R(\theta)$$

and the residual strain x_1 by

$$x_1(\theta) = \frac{S_1(\theta)}{n_2} = \frac{f_1(\theta) + f_2(\theta)}{n_2}$$

On cooling η_1 has no effect on the R/temperature curve because the residual stress has relaxed to be equal to the sum of the yield values at the highest temperature attained and the R/temperature curve for cooling is given by:

$$R(\theta) = S_1(\theta_m) - f_2(\theta)$$

where $S_1(\theta_m)$ is the residual stress remaining at the highest temperature θ_m attained. The complete equations for the R/temperature curve are:

$$\begin{aligned} R(\theta) &= 0 \quad S \leqslant f_2(\theta) \\ R(\theta) &= S - f_2(\theta) \quad f_1(\theta) + f_2(\theta) > S > f_2(\theta) \\ R(\theta) &= f_1(\theta) \quad S \geqslant f_1(\theta) + f_2(\theta) \end{aligned}$$

for rising temperatures, and

$$\begin{aligned} R(\theta) &= S_1(\theta_m) - f_2(\theta) \quad S_1(\theta_m) > f_2(\theta) \\ R(\theta) &= 0 \quad S_1(\theta_m) < f_2(\theta) \end{aligned}$$

for subsequent falling temperatures.

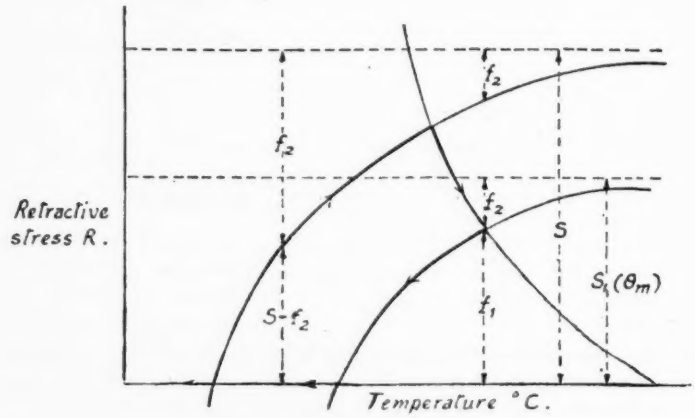

FIG. 6

Figure 6 shows the R/temperature curve obtained according to the above equations, assuming the shape of the yield value temperature curve. The curve of Figure 6 bears a close resemblance to the experimental curve of Figure 3 except that, in Figure 3, the cooling curve is not parallel to the heating curve. This is probably due to the neglect of thermal contraction[5] of both the P.V.C. and brass strip. If values for the coefficients of thermal expansion are known, it should be possible by suitable design of experiment to obtain curves of the type shown in Figure 6 if the proposed theory is correct.

It is easy to see how the presence of a yield value in η_2 accounts for the percentage retraction/temperature curve. In this case η_1 has no effect whatsoever. The percentage retractions, p, at some temperature θ is given by:

$$p = \frac{x - x_1(\theta)}{x} 100$$
$$= \frac{S - f_2(\theta)}{S} 100 \qquad S > f_2(\theta)$$
$$p = 0 \qquad S < f_2(\theta)$$

giving a curve similar to that shown in Figure 2.

In terms of molecular structure the yield values f_1 and f_2 may have the following significance. Before chain uncurling (D_{HE}) and interchain sliding ($D_{\mathrm{VISC.}}$) can take place certain minimum stresses, which fall with increasing temperature, must be exceeded. This requires that Equation (1) be modified to:

$$D = \frac{S}{\eta_1} + \frac{S - f_2}{\eta_2}(1 - e^{-(\eta_2/\eta_2)t}) + \frac{S - f_1 t}{\eta_1}$$

In the simple theory of the calender effect proposed here, one dimension alone—the direction of calendering—has been considered.

It is clear that the extension of the theory to three dimensions would present no novel features.

SUMMARY

The facts relating to the calender effected are briefly stated and illustrated by experimental data obtained with calendered plasticized polyvinyl chloride sheet. The nature of rubberlike deformation is outlined. A theory of the calender effect is proposed in terms of a mechanical model whose relation to molecular structure is indicated. The theory postulates that temperature-dependent yield values be associated with the mechanisms of high elastic deformation and plastic flow.

ACKNOWLEDGMENT

Thanks are due to the Directors of Callender's Cable & Construction Company, Limited, in whose laboratories the experimental work was carried out, for permission to publish this paper, and to E. Tunnicliff and I. K. Fisher for helpful discussions.

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[5] For over the path AB (see Figure 3) the experimental values obtained for R will be lower than those given by the model by an amount that increases with increase in temperature. The path BC, however, is independent of thermal expansion effects, R being controlled solely by f_1, and any stresses that might now be set up by thermal expansion will be dissipated by the flow that would take place in η_1. On cooling, two effects occur, of which the path CDE is the resultant. The model requires that this path fall to zero parallel to AB, while, owing to thermal contraction a continually increasing stress has to be exerted to keep the strip at constant length.

THE CHEMICAL CONSTITUTION OF BUTADIENE RUBBERS, BASED ON THE FORMIC ACID AND FORMALDEHYDE IN THE DECOMPOSITION PRODUCTS OF THEIR OZONIDES *

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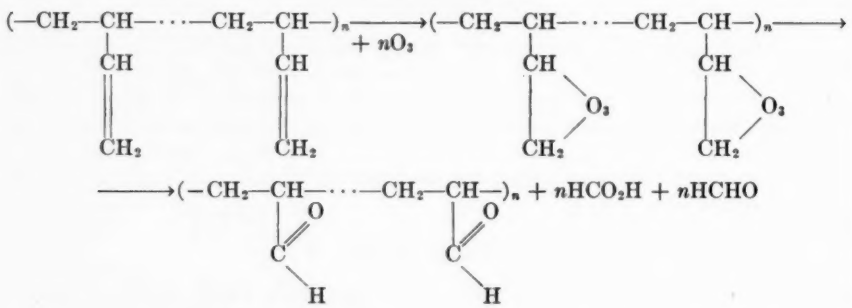
In the field of research concerned with the synthesis of new types of butadiene rubbers, there has arisen the necessity of a rapid and simple method for determining the chemical constitution of these rubbers. In the present work, the vinyl group was selected to characterize the structure of various butadiene rubbers because it forms combinations of molecules with butadiene in the 1,2-position (system of Ziegler[1]). Decomposition of rubber ozonides, the molecules of which contain vinyl groups, as well as other carbon groups, leads to the formation of formic acid and formaldehyde.



For each molecule of formic acid and each molecule of formaldehyde formed in the decomposition products, one vinyl group is present in the original rubber molecule. Therefore, a quantitative determination of formic acid and formaldehyde in the decomposition products of the ozonides indicates the number of vinyl groups.

The analytical method developed in the present work is in principle as follows:

The rubber is freed of impurities by precipitating it two or three times from its benzene solution, and is dried in a vacuum at a temperature not higher than 30°C. To prevent any possible oxidation of the rubber, all preliminary steps in the ozonization process should be carried out in an atmosphere of nitrogen containing no oxygen. In this experiment, two to three grams of purified rubber is sufficient, and this is ozonized in the form of a one per cent solution in

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by F. C. Davis from the *Zhurnal Prikladnoy Khimii (Journal of Applied Chemistry*, U.S.S.R.), Vol. 17, No. 3, 1944, pages 107–113. U. A. Borgman, N. E. Ushakova, O. M. Simonoba and K. M. Kontorovich collaborated in the experimental part of the investigation.

chloroform. The carbon content of the sample is determined by calcining the sample with black copper oxide. Ozonization is carried out by means of a mixture of oxygen and ozone (five to six per cent ozone) at −20°C. The rate of the flow of these gases is 20 liters per hour. The completion of ozonization can be determined accurately by comparing the concentrations of ozone in the gaseous mixture in the reactor and in that issuing from it. The concentration of ozone is determined by titration with sodium thiosulfate of the iodine which has been liberated from a solution of potassium iodide during passage through it of the ozonized oxygen for a definite period. After completion of ozonization, the solvent (chloroform) is removed by a vacuum at 20°, and the remaining ozonide washed with ether for 15–20 hours. This extraction with ether reduces to a great extent the tendency of the ozonide to decompose explosively[2]. The ether is then evaporated; the ozonide is again dried under the same conditions for two hours more. Following this, 7 times its weight of water is added, and the mixture is decomposed on a water-bath by carefully heating it until it

TABLE 1

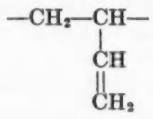
RESULTS OF A STUDY OF VARIOUS RUBBERS

No.	Character of Rubber	Elementary analysis %C	Elementary analysis %H	Purified rubber for ozonization (g.)	Determination of formic acid: Yield (g.)	Determination of formic acid: Total solution (g.)	Determination of formaldehyde: Yield (g.)	Determination of formaldehyde: Total solution (g.)
1	Sodium-butadiene rubber (rod method)	87.54	11.08	5.89	0.1590 0.1584	1.587	0.00535 0.00552	0.543
2	Sodium-butadiene rubber (without rods)	87.66	11.06	4.52	0.1650 0.1676	1.109	0.00344 0.00352	0.348
3	Rubber obtained by homogeneous polymerization	88.31	11.21	2.98	0.0995 0.0995	0.746	0.00162 0.00156	0.119
4	Rubber obtained from latex (Type DAB)	88.33	11.31	4.46	0.1351 0.1339	0.897	0.00182 0.00176	0.179
5	Rubber obtained from latex (Type G-54)	87.17	10.98	6.36	0.1265 0.1258	1.262	0.00087 0.00087	0.130
6	Lithium-butadiene rubber (polymerized at 60°)	87.14	11.00	5.97	0.0980 0.0977	0.978	0.00096 0.00088	0.138
7	Potassium-butadiene rubber (polymerized at 60°)	87.33	11.16	6.53	0.1496 0.1500	1.498	0.00233 0.00223	0.342
8	Sodium-butadiene rubber (polymerized at 60°)	87.75	11.05	5.95	0.1608 0.1608	1.608	0.00246 0.00258	0.378
9	Sodium-butadiene rubber (polymerized at 60° in presence of solvent—2-butene)	88.72	11.44	4.46	0.1674 0.1670	1.114	0.00352 0.00338	0.345
10	Sodium-butadiene rubber (polymerized at 60° in presence of solvent—petroleum-ether)	88.28	11.28	4.44	0.1680 0.1677	1.118	0.00330 0.00336	0.333
11	Sodium-butadiene rubber (polymerized at 22°)	87.63	11.13	2.91	0.1618 0.1630	1.137	0.00264 0.00276	0.189
12	Butadiene-styrene copolymer from latex (Type DAB)	88.81	10.45	4.43	0.1498 0.1494	0.997	0.00122 0.00110	0.116
13	Butadiene-styrene copolymer from latex polymerized with benzoyl peroxide	89.50	10.00	4.45	0.1599 0.1634	1.077	0.00098 0.00092	0.095
14	Butadiene-styrene copolymer from latex-homogeneous polymerization	88.93	10.59	4.24	0.1103 0.1106	1.104	0.00096 0.00092	0.094

boils. The contents of formic acid (by the calomel method of Finke[3]) and of formaldehyde (by condensation with β-naphthol by the method of Fosse, de Graeve and Thomas[4]) in the solution of the decomposition products are determined. Both methods were repeatedly checked[5], and it is believed that they are sufficiently accurate and convenient for the work concerned.

In this way, a series of synthetic butadiene rubbers, especially prepared under various conditions of polymerization, were studied. The percentage of carbon skeleton recovered as formic acid and formaldehyde in the decomposition products of the ozonide was multiplied by 4, since each molecule of formic

acid or formaldehyde unites with only one out of four carbon atoms in the chain:



In this way the percentage of vinyl groups in the chains of the rubber molecule was computed. The results of an investigation of several rubbers are shown in Tables 1 and 2.

TABLE 2

CHEMICAL CONSTITUTION OF SOME RUBBERS, BASED ON THE CONTENT OF ATTACHED VINYL GROUPS

No.	Character of Rubber	Percentage of carbon skeleton of rubber found as HCOOH	HCOH	HCOOH +HCOH	Percentage of vinyl bonds in the rubber molecule
1	Sodium-butadiene rubber (rod method)	8.03	4.21	12.24	48.96
2	Sodium-butadiene rubber (without rods)	7.31	3.52	10.83	43.32
3	Rubber obtained by homogeneous polymerization	7.50	1.85	9.35	37.40
4	Rubber obtained from latex (Type DAB)	5.94	1.82	7.76	31.04
5	Rubber obtained from latex (Type G-54)	5.94	0.94	6.88	27.52
6	Lithium-butadiene rubber (polymerized at 60°)	4.91	1.06	5.97	23.83
7	Potassium-butadiene rubber (polymerized at 60°)	6.86	2.40	9.26	37.04
8	Sodium-butadiene rubber (polymerized at 60°)	8.04	2.90	10.94	43.76
9	Sodium-butadiene rubber (polymerized at 60° in presence of solvent—2-butene)	7.35	3.48	10.83	43.32
10	Sodium-butadiene rubber (polymerized at 60° in presence of solvent—petroleum-ether)	7.45	3.40	10.85	43.40
11	Sodium-butadiene rubber (polymerized at 22°)	11.55	3.31	14.86	59.44
12	Butadiene-styrene copolymer from latex (Type DAB)	6.78	1.12	7.90*	31.60
13	Butadiene-styrene copolymer from latex polymerized with benzoyl peroxide	7.06	0.96	8.02*	32.08
14	Butadiene-styrene copolymer from latex—homogeneous polymerization	7.64	1.00	8.64*	34.56

* Calculation based on the entire carbon skeleton.

The data in Tables 1 and 2 show the influence of different conditions of polymerization on the chemical constitutions of a few rubbers. The percentages of carbon skeleton recovered as formic acid and formaldehyde from different rubbers ranged from 5.97 to 14.86 per cent. This corresponds to percentages of 23.88 to 59.44 for the vinyl group (see Table 2).

According to the content of bonds with the vinyl group, the rubbers which were studied may be arranged in the following order, depending on the method

by which they were prepared: sodium-butadiene rubber, obtained from polymerization by the rod method, characterized by a high content of bonds with the vinyl group, *i.e.*, 48.96 per cent; rubber obtained by polymerization without the use of rods has a somewhat smaller content of such bonds. With respect to rubbers from latex, prepared as Type DAB and Type G-54, the percentage of vinyl group bonds is not large, *viz.*, 31.04 and 27.50 per cent, respectively. Rubber obtained by homogeneous polymerization is intermediate between rubbers from latex and from sodium-butadiene without the use of rods, and contains 27.40 per cent bonds.

The influence of an alkaline metal on the chemical structure of rubber is shown in the following experiments. In these experiments polymerization was conducted at 60° in an ampoule. Lithium-butadiene rubber was found to contain the smallest percentage of bonds of vinyl groups (23.88 per cent). Potassium-butadiene rubber had a higher content of vinyl groups (37.04 per cent) and sodium-butadiene rubber a still higher content (43.76 per cent). In the case of sodium-butadiene rubber, obtained by polymerization at 60°, it was also established that polymerization in the presence of a solvent (2-butene or petroleum ether) has no influence on the content of vinyl groups in the resulting rubber.

This polymerization process without heating (at 22° C) obviously raises the percentage of vinyl groups (from 43.76 to 59.44 per cent).

TABLE 3

No. of Sample	Type of rubber	Percentage of carbon skeleton of rubber recovered as			Percentage of vinyl bonds in the rubber molecule
		HCOOH	HCOH	HCOOH +HCOH	
1	Rubber obtained by homogeneous polymerization	7.41	1.82	8.23	36.92
	Same, repeated	7.58	1.89	9.47	37.88
2	Sodium-butadiene rubber (polymerized at 20°)	11.68	2.98	14.66	58.64
	Same, repeated	11.41	3.64	15.05	60.20
3	Butadiene-styrene rubber from latex (Type DAB)	6.63	1.18	7.81	31.24
	Same, repeated	6.93	1.07	8.00	32.00

Formic acid and formaldehyde were also found in the decomposition products of ozonides of butadiene-styrene rubbers. This leads to the conclusion that in this case also, independent of the method of polymerization, whether as an emulsion or as a homogeneous medium, a part of the butadiene groups unite in 1,2-position (about 31.5–34.5 per cent calculated on the carbon skeleton). To verify these results, several samples were checked (see Table 3).

The data show that the difference in percentages of carbon skeleton recovered as formic acid and formaldehyde in two parallel investigations does not exceed 0.4 per cent (absolute) or 1.6 per cent based on the content of vinyl groups.

The possibility of partial oxidation of chloroform to formic acid and formaldehyde by ozone[6] and the influence of this oxidation on the results of the determination led the present authors to carry out special experiments, whereby it was proved that the amounts of formic acid and formaldehyde formed in this manner are very insignificant, and the lower the temperature of the reaction the smaller they are.

These latter experiments showed also that, by vacuum distillation, *i.e.*, distilling the chloroform from the ozonide, formaldehyde, as well as formic acid, is completely driven off, with the chloroform.

Finally, while investigating one of the rubbers, it was proved that prolonged passage of ozone through the reaction mixture after all the polymer had been ozonized, and also the addition to chloroform after ozonization of a definite quantity of pure formic acid, as was done in another experiment, does not result in any different yields of formic acid and formaldehyde in the decomposition products from the yields obtained under ordinary conditions.

From these experiments it follows that partial decomposition of chloroform by ozone does not affect in any significant way the results of the determination. Taking into account these facts, it appears that the formic acid and formaldehyde in the solution of the decomposition products of ozonide are formed solely as decomposition products of the rubber ozonide.

The results obtained in the present investigation indicate that the proposed method for determining the characteristic chemical structure of butadiene rubbers makes it possible to establish the relation between the properties of these rubbers and their structure, and may possibly be of use in improving the quality of rubber and in synthesizing new types of butadiene rubbers with novel and valuable properties.

CONCLUSION

A rapid method has been developed, with the aid of several types of synthetic rubber, for determining the characteristic chemical structure of butadiene rubbers by means of the formic acid and formaldehyde recovered when their ozonides are decomposed.

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PREPARATION OF 2,3-DIMETHYLBUTADIENE AND ITS POLYMERIZATION TO "METHYL RUBBER" *

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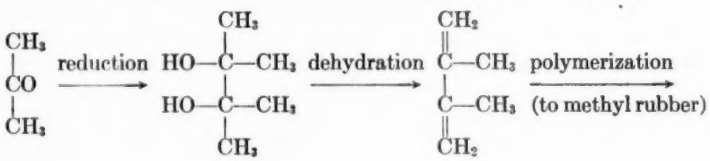
Between 1915 and 1918 the Bayer Company in Germany produced over 2,500 tons of rubber from 2,3-dimethylbutadiene. The product, called "methyl rubber", was not a commercial success. Its tensile strength was low and it suffered from the further drawback of being very susceptible to oxidation, as a result of which it was converted into a sticky resinous material. It is of interest to note that at this period the beneficial effect of carbon black on the tensile strength of rubbers was not known, nor had the antioxidative properties of such chemicals as β-naphthol, nitronaphthalene and bipiperidyl been discovered. In the light of this knowledge the authors considered that a reinvestigation of the properties of "methyl rubber" might be of interest. The preparation of the methyl rubber from acetone is described in the following account.

The procedure was that illustrated in the following scheme:



(acetone) (pinacone) (dimethylbutadiene)

The first stage, the reduction of acetone to pinacone, was carried out initially as already described[1], using magnesium amalgam as the reducing agent. This method was later discarded in favor of an electrolytic reduction method, which proved more simple in operation and led to improved yields of pinacone. Electrolytic methods have been described by Tafel[2] and by Wilson and Wilson[3]. The former employed a lead cathode in an acid electrolyte, and observed the formation of some pinacone, but this was incidental, since the paper deals mainly with the formation of organic lead compounds under these conditions. The work of Wilson and Wilson deals with the reduction of acetone in alkaline media at a mercury cathode. Attempts to reproduce their results proved abortive, none or only small amounts of pinacone being formed under the conditions employed by them.

The reduction of acetone can give rise to one or all of three products, *viz.*, propane, isopropyl alcohol and pinacone. The use of cathodes at which the hydrogen overvoltage is high, *e.g.*, cadmium, leads to the formation of large

* Reprinted from the *Proceedings of the Royal Irish Academy*, Vol. 50, Section B, No. 10, pages 219–225 March 1945.

amounts of propane. Cathodes of somewhat smaller hydrogen overvoltage, *e.g.*, lead, tend to cause a less vigorous reduction of the acetone and so produce much isopropyl alcohol. The conversion of acetone to pinacone represents a very mild form of reduction, and points to the choice of a cathode somewhat lower in the hydrogen overvoltage series than lead. Such a cathode was evolved by the addition of a small amount of tin to lead in the form of an alloy[4]. With this cathode and a catholyte of pure dilute sulfuric acid, yields of pinacone higher than any recorded in the literature have been obtained. An interesting observation here is that the use of the pure acid is essential. The substitution of ordinary commercial acid was found to yield little or no pinacone. There is evidence to suggest that traces of arsenic in the electrolyte are responsible for this negative result. Reduction with cathodes of tin and of lead-copper were also investigated. The results obtained are shown in the following table.

Cathode	Yield of pinacone (%)	Yield of isopropyl alcohol (%)	Current efficiency (%)
Tin	35	12	10
Lead-tin	46	45	89
Lead-copper	23	38	80

The current efficiency is here the overall current efficiency, and represents the fraction of the current employed in the reduction of the acetone, whether to pinacone or isopropyl alcohol. A point of theoretical interest in connection with the use of the lead-tin cathode was that the high current efficiency above was only reached after reduction had been in progress for some time. The initial current efficiency was very low, but this kept increasing until it reached its maximum after an hour. This phenomenon may have to do with the previous formation of a lead-tin hydride or the building up of a monomolecular layer of atomic hydrogen around the cathode. It is proposed to study this interesting effect more closely. Another point requiring investigation is the effect of copper ions in the solution. Our Pb-Sn cathodes were made by "tinning" a thin layer of the alloy on a copper gauze. The anodic treatment described below occasionally caused the thin coating of alloy to dissolve in places so that the underlying copper was dissolved. In the subsequent electrolytic reduction copper ions made their way to the cathode. This did not appear to lessen pinacone production, and may have improved it, but a study of the effect of copper on the reduction was postponed.

For the dehydration of pinacone to dimethylbutadiene, various catalysts such as hydrobromic acid[5] and potassium hydrogen sulfate were used, but the results were not satisfactory because of the coformation of considerable quantities of pinacoline from the pinacone by the well-known intramolecular rearrangement. The best results were obtained with activated aluminum oxide, which is much used in the dehydration of alcohols and possesses the advantage of not causing shifting of double bonds. By passing the vapor of pinacone over a layer of this oxide at 450° C, dimethylbutadiene was obtained in a yield of 74 per cent of the theoretical. Polymerization of the dimethylbutadiene was carried out by heating in a sealed tube for two months at a constant temperature of 70° C. During this time the liquid gradually became more viscous until finally it had the appearance of a firm jelly. A report by Messrs. Dunlop's, Cork, on the properties of this rubber will be found at the end of this paper.

EXPERIMENTAL

Electrolytic Reduction of Acetone to Pinacone.—From preliminary experiments it became apparent that two factors had an important bearing on the success of the reduction, *viz.*, the purity of the electrolyte and the use of a diaphragm of low electrical resistance and low permeability. A porous pot with these properties was procured from Messrs. Doulton, London. The cathode was prepared by coating a copper gauze with an alloy consisting of electrolytic lead, 90 parts, and Analar tin, 10 parts. The gauze was first degreased by immersion in a strong solution of sodium hydroxide, then washed free of alkali with distilled water, and immersed for a few seconds in a solution of zinc chloride. It was then dipped in the molten lead-tin alloy forming a plate with roughened surface. This plate was perforated so as to allow free circulation of the electrolyte.

Before proceeding to the reduction stage it was found desirable to submit this cathode to a preliminary treatment which consisted in making it the anode of an electrolytic cell, the electrolyte being a 20 per cent solution of sulfuric acid (B.D.H.As.T.) and the cathode a rod of pure lead. A current of 0.5 ampere was passed through the cell for 30 minutes. By this preliminary treatment the surface of the lead-tin electrode was made spongy in appearance.

The apparatus used in the reduction of the acetone was so constructed that the hydrogen evolved during an experiment could be measured and the current efficiency calculated. The prepared cathode, in the shape of a cylinder, was placed in a beaker and surrounded the porous pot in which was placed a rod of pure lead as anode. The beaker carried a tight-fitting rubber-cork with four holes, two of which carried the leads for the anode and cathode, the third a thermometer and the fourth hole a vertical condenser, to which was attached a delivery tube for the collection of the hydrogen evolved over water. The cathode space contained 110 cc. of 20 per cent sulfuric acid, to which was added 110 cc. of acetone. The anolyte was 70 cc. of 10 per cent sulfuric acid. A current of 1.5 amperes was passed through the cell, corresponding to a current density of approximately 1.5 amperes per sq. dcm. During the experiment the temperature was not allowed to rise above 20° C. At the commencement the current efficiency was only 9 per cent, but this kept increasing until, at the end of an hour, it had increased to a maximum of 89 per cent. The theoretical amount of electricity required to reduce the acetone to pinacone was 40.5 ampere-hours. A total quantity of 49 ampere-hours was passed through the cell. At the end of the experiment a quantity of pinacone hydrate had crystallized out, and most of the sulfuric acid had gone to the anolyte. The catholyte was filtered and the filtrate rendered neutral by addition of sodium carbonate. It was then distilled through an evaporator column until all isopropyl alcohol and unchanged acetone had been removed. The residual liquid when left in the ice chest over night deposited crystals of pinacone hydrate. This was collected and dried at room temperature. The total pinacone hydrate weighed 56 grams. Allowing for recovered acetone (33 cc.) (see below) this represents a yield of pinacone of 46.2 per cent.

The estimation of the acetone and isopropyl alcohol in the distillate was carried out as follows. The acetone was determined by conversion to iodoform and titration of the excess of iodine as recommended by Stahly, Asburn and Werkmann[6]. Under the conditions employed by these authors the isopropyl alcohol present was unaffected. For the determination of the isopropyl alcohol, an aliquot portion of the distillate was oxidized with bichromate and

sulfuric acid as recommended by Adams and Nicholls[7], thus converting the isopropyl alcohol to acetone. The acetone was removed by distillation and redetermined in the distillate as above. The increase in the acetone is a measure of the quantity of isopropyl alcohol in the original mixture.

Dehydration of Pinacone to 2,3-dimethylbutadiene.—The pinacone hydrate was heated in a flask carrying an evaporator column until the thermometer in the column registered a temperature of 115° C, at which temperature anhydrous pinacone remained.

The catalyst for the dehydration of the pinacone was prepared by gently heating aluminum nitrate until all traces of oxides of nitrogen had been expelled. The residue was then further heated in a vacuum at a temperature of 160° C for five hours. The product was coarsely powdered and sieved so as to remove all finer and larger particles of oxide. A Pyrex tube, 110 × 2.2 cm., packed with this aluminum oxide, was enclosed for 70 cm. of its length in a larger Pyrex tube of 3.5 cm. diameter. There were two windings on the latter of 24 S.W.G. nichrome resistance wire. These windings were connected up in parallel and controlled by an external resistance. A thermocouple, connected to a pyrometer indicating outfit, was inserted in the space between the two tubes. The outer tube was covered with a layer of asbestos. The heating elements were connected to the 220-volts supply and the temperature controlled by means of the external resistance. One end of the inner tube was fused to the side tube of a small distilling flask. The other end was connected by means of ground glass joints to two receivers placed in series which were surrounded by a freezing mixture of solid carbon dioxide and ether. The apparatus was connected with the water pump, and a gentle suction was maintained during the course of an experiment. The electric furnace was heated to a temperature of 470° C, as recorded by the pyrometer, and, when regulated to this temperature, 100 grams of anhydrous pinacone were allowed to flow into the distilling flask, which was immersed in an oil bath maintained at a temperature of 180° C. The pinacone was allowed to flow in at such a rate that the duration of the experiment did not exceed six minutes. The contents of the two receivers were united, and the water layer was removed in a separating funnel. The crude dimethylbutadiene, after drying over anhydrous potassium carbonate, was distilled through an evaporator column, and the fraction having a boiling point range of 69° to 70° C was collected. This fraction, which was almost pure dimethylbutadiene, weighed 52 grams, representing a yield of 74 per cent of the theoretical.

Polymerization of 2,3-dimethylbutadiene to "Methyl Rubber".—The dimethylbutadiene was heated in a sealed tube which was completely immersed in an oil bath, the temperature of which was kept at 70° C by means of an electrically operated control. It was observed that, after two weeks at this temperature, the liquid had become slightly viscous. The heating was continued until the viscosity of the liquid did not appear to increase. The time taken for this was eight weeks. At the end of this period a highly viscous product was formed, which, when cooled to room temperature, had the appearance of a clear jelly.

The quantity of methyl rubber prepared by us did not permit any extensive investigations of its physical properties. A sample was forwarded to the Irish Dunlop Co., Cork, and we are indebted to them for permission to publish the following report.

"Ten per cent of the methyl rubber was incorporated into our standard Compound No. 884. Following cure of 45 minutes at 280.5° F, the physical properties were as follows.

Tensile strength	1.60	kg. per sq. mm.
Elongation at load of 0.5 kg. per sq. mm.	361	per cent
Elongation at break	666	per cent
Permanent set	8.3	per cent
Durometer hardness (Shore)	47	

These figures are in line with standard compound readings. Due to smallness of sample, it was not possible to make up a 100 per cent compound. The figures above do not indicate performance in service, as a considerable quantity of material would be required to ascertain this."

It will be seen from this report that incorporation of 10 per cent of the methyl rubber into a standard rubber compound had no harmful effects on the physical properties of the rubber.

We do not at present intend to proceed further with the work, as the emergency conditions which rendered it desirable two years ago to investigate the possibility of making synthetic rubber in this country from native materials have now largely disappeared.

ACKNOWLEDGMENT

We are indebted to the Emergency Scientific Research Bureau for a grant towards the expenses of the work described in this paper, and for permission to publish it.

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THE INTERACTION OF PLASTICIZERS AND POLYMERS *

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The general problem of plasticizer polymer systems has two distinct aspects. The choice of a suitable plasticizer for use with a given polymer is first influenced by the degree of miscibility which is obtainable. Given sufficient miscibility, i.e., given a minimum compatibility, plasticizers will then be chosen for their efficiency in conferring specific properties. The efficiency of a plasticizer can simply be measured by the amount which is required to produce a certain degree of plasticity or softness in the plasticizer-polymer mixture. This paper deals only with the problem of plasticizer compatibility; its aim is to show how compatibilities can be measured, and to consider briefly the physical factors which determine good compatibility. Correlations between the chemical structure of a plasticizer and its compatibility properties are not considered. The scope is further limited to amorphous polymers on the one hand and liquid plasticizers on the other. We shall assume that the polymer and plasticizer are in thermodynamic equilibrium: the formal problem of determining the compatibility is then simply that of determining the mutual solubility relationships of a polymer and a simple liquid, and requires a brief discussion of the equilibrium between a polymer and a liquid, which is, in general, a solvent or swelling agent.

NATURE OF THE INTERACTION

Since we assume that the polymer and plasticizer are in thermodynamic equilibrium, we can apply the current theories of polymer solutions. The equilibrium conditions are determined by the value ΔG of the Gibbs' free energy change on passing from the original amorphous polymer to the swollen or dissolved state. The configurational increase in entropy corresponding to this change is large, and has been calculated by Flory[1], Huggins[2] and Guggenheim[3], with essentially similar results. If all the solvents or swelling agents considered have molecules roughly of the same size relative to that of the polymer chain link, the configurational increase in entropy on mixing is the same for all liquids. Thus variations in the equilibria found with different liquids must be ascribed entirely to differences in the heats of mixing. Since a direct calorimetric measurement of ΔH, the change in heat content on mixing, is very difficult, heats of mixing are usually derived from measurements of the vapor pressure or osmotic pressure of the system over a range of temperature. Very few systems have been measured; as a general rule the heat changes are found to be small. In the rubber-benzene[4] system a small amount of heat is absorbed on mixing (ΔH small and positive), rubber and toluene[5] mix almost without heat change; when there are attractive forces acting between the polymer and solvent, heat is evolved on mixing, as in the systems

* Reprinted from the *Transactions of the Faraday Society*, Vol. 41, No. 2, pages 90–101, February 1945.

nitrocellulose-acetone[6] and cellulose acetate-tetrachlorethane[7]. While differences in ΔH determine the differences in equilibrium states, the large swellings and high solubilities found in polymer systems are due mainly to the very large increase of entropy on mixing and not to big attractive forces between the polymer and liquid concerned.

If, then, the polymer mixes with the plasticizer without heat change, or if there are attractive forces acting between them, there should be complete miscibility over the whole range of composition, as the heat effect is acting with the entropy effect to promote solution. But if the plasticizer is to some extent repelled by the polymer, heat is absorbed on mixing, and this adverse heat effect may be large enough to produce phase separation and the limited swelling effects which are often found. A quantitative treatment of these phenomena was first given by Flory[1], and was worked out in detail by Guggenheim[3]. The condition for phase separation is, generally, that w/kT should be positive and greater than some critical value not markedly dependent on the polymer chain length: w is here a measure of the interaction energy between the plasticizer or solvent molecule and the polymer chain link. It has a value of zero if the polymer and solvent mix without heat change and is negative if there is polymer solvent attraction. Positive values of w correspond to polymer solvent repulsion. It is clear then that the formation of well-defined complexes, or stoichiometric compounds, is not necessary for good compatibility. In the extreme case large attractions between the polymer and plasticizer may lead to the formation of a solvated hull in a simple chemical ratio. This appears to be the case in the system nitrocellulose-acetone where calorimetric measurements of Kargin and Papov[8] have suggested that a 1:1 complex is formed. In general, however, good compatibility is found when the forces between the polymer and plasticizer correspond to attraction or even slight repulsion. Comparative compatibility values should, therefore, be obtained from a comparative study of the heats of mixing or interaction forces between a polymer and a series of plasticizers.

MEASUREMENT OF THE INTERACTION

Any type of experiment which measures directly or comparatively the interaction or attractive forces between a polymer and a series of plasticizers is thus suitable for estimating relative compatibilities. The obvious comparative method would be to measure the equilibrium swelling of a cross-linked or otherwise insoluble specimen of the polymer in a series of plasticizers: this method has the advantage of allowing controllable measurements over a range of temperature. It has been used successfully in the case of synthetic rubbers, but polymers like cellulose acetate, polyvinyl chloride or polystyrene reach equilibrium very slowly when swollen in the form of sheet or thin films, and the method seems to require modification. It is obviously unsuitable when the polymer is soluble in the plasticizer. Direct measurement of the heats of mixing of polymers and plasticizers is difficult, but some advance is being made using a suitable monomer as a model for the polymer link. This point is referred to later. Apart from swelling or calorimetric methods, however, it was suggested in an earlier paper[9] that polymer solvent interactions and possibly comparative swelling results could be obtained from a study of the usual $\eta_{sp}/c - c$ viscosity curve obtained from measurements in dilute solution. Experiments on polymer-plasticizer systems described here confirm the general prediction, although the exact form of the relationship is still admittedly not

clear. The experiments are based on the following general considerations, which are at least qualitatively correct.

1. The increase of the η_{sp}/c ratio with concentration, *i.e.*, the initial slope of the $\eta_{sp}/c - c$ curve, is a function of the solvent. If the solvent is attracted by the polymer chains, *i.e.*, if ΔH or w is negative, extended configurations of the polymer chains occur, there is increasing interaction between the chains as the concentration increases, and both the limiting ratio at zero concentrations $[\eta]$ and the slope of the $\eta_{sp}/c - c$ curve will be high. If there is polymer solvent repulsion, coiled up polymer configurations reduce $[\eta]$ and the slope of the curve. The theory originally suggested that the slope (but not the limiting intercept) of the $\eta_{sp}/c - c$ curves was a linear function of $w/\boldsymbol{k}T$.

2. Frequently the polymer is insoluble in the plasticizer or liquid in question, and in this case comparative measures of the interaction can be directly obtained from swelling measurements. It is possible also to use viscosity results, provided the measurements are made in carefully chosen mixed solvents. Suppose that a polymer P is dissolved in a solvent S_1 without any heat effects, so that $w_{PS_1} = 0$. If a second liquid or plasticizer S_2 is added to the solution, it is reasonable to suppose that it interacts to the same extent both with a polymer link and a single molecule of the type S_1. We can then imagine that this single interaction (which we may call w) is responsible for any variations we may find in the viscosity curves. If then we have a dilute solution of polymer P in S_1 and add varying amounts of S_2, we should get a series of $\eta_{sp}/c - c$ curves whose slopes and intercepts are functions both of the interaction w and the amount of S_2 in the mixture. If, for comparative purposes, measurements are made with a fixed solvent composition, the curves should give a directly comparative measure of polymer-S_2 (plasticizer) interaction. In the experiments described below S_1 is the solvent chosen as far as possible to comply with these conditions and S_2 the added plasticizer, whose relative compatibility will be related to the slopes of the $\eta_{sp}/c - c$ curves.

EXPERIMENTAL METHODS AND RESULTS

Nonsolvent Plasticizers.—If the polymer is not completely soluble in the plasticizer, a direct experimental comparison can be made between viscosity results and swelling data. If the slope of the $\eta_{sp}/c - c$ curve for a given plasticizer content in the mixed solvent depends only on w, there should be some correlation between this slope and the equilibrium swelling of the insoluble polymer in the pure plasticizer. Swelling data are, however, only reliably obtained for vulcanized rubbers, and we have first tested this prediction with the aid of Gee's published results[10] on the swelling of lightly vulcanized synthetic rubbers. The swelling liquids used were simple aliphatic esters: while these are not plasticizers in the usual sense, they are chemically sufficiently similar to the more usual type to serve as test liquids in systems where strong dipole forces do not exist. The results are given below for the system Neoprene-benzene-plasticizer. We assume that benzene is a suitably "indifferent" solvent for the polychloroprenes which form the basis of the Neoprene type of synthetic rubber: results given later in this paper show, however, that small deviations from this state do not invalidate the main conclusions. Gee measured the swelling of lightly vulcanized discs of Neoprene in a series of liquids, and found that the results fitted a curve determined by the cohesive energy densities (E_s/V_s) of the esters used. These results indicate that the interaction between the ester and Neoprene is small or corresponds to a slight

repulsion and we might expect, as is found in practice, that many of the pure esters do not completely dissolve unvulcanized specimens of rubber. We have in effect, then, a series containing some nonsolvent plasticizers. Dilute solutions of unvulcanized specimens of Neoprene were prepared, using as solvents 50%-by-volume mixtures of benzene and the corresponding ester: the viscosity of each solution was measured in a standard Ostwald viscometer at 25° C (±0.02° C) relative to the appropriate solvent mixture. The increase of the

TABLE I

SWELLING AND VISCOSITY RELATIONSHIPS. NEOPRENE-GN

Neoprene-GN-benzene +	Intercept $[\eta]$	Slope	Q	$(E_S/V_S)^{\frac{1}{2}}$ (cal./cc.)$^{\frac{1}{2}}$
Heptane	0764	14	0.24	7.50
Isobutyl *n*-butyrate	0920	82	2.27	7.78
Butyl *n*-butyrate	0965	96	2.60	8.06
Butyl acetate	0914	82	2.23	8.53
Propyl acetate	0890	72	1.82	8.75
Ethyl acetate	0798	50	1.14	9.08
Ethyl tormate	0718	36	0.51	9.43
Methyl acetate	0649	22	0.49	9.58

viscosity ratio η_{sp}/c with the concentration was measured for each solution: over the range of polymer concentration 0–0.4 g./100 cc., this increase was linear and the slope of the $\eta_{sp}/c - c$ curve was readily found. Both the limiting intercept $[\eta]$ of the η_{sp}/c ratio at zero concentration and the slope of the curve depended on the solvent. The results are given in Table I together with Gee's figures for the equilibrium swelling Q in the pure ester and the corresponding E_s/V_s value of the ester itself.

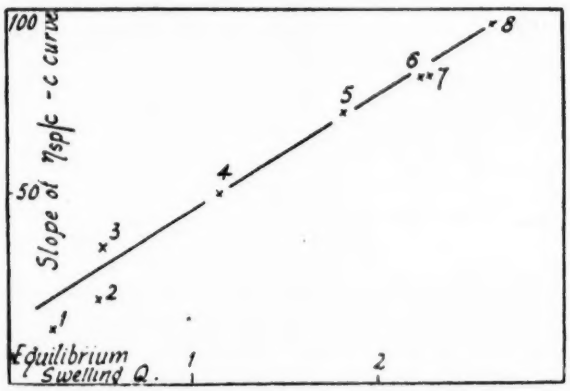

FIG. 1.—Relationship between viscosity and equilibrium swelling for Neoprene-GN in a series of liquids. Viscosity measurements in 50%-by-volume mixtures with benzene.
Liquids.—1. Heptane. 2. Methyl acetate. 3. Ethyl formate. 4. Ethyl acetate. 5. Propyl acetate. 6. Butyl acetate. 7. Isobutyl butyrate. 8. Butyl butyrate.

The plots of the limiting intercept $[\eta]$ and the slope of the curves against the corresponding Q values are surprisingly good straight lines. Figure 1 shows the plot of Q against the initial slopes of the viscosity curves: this plot corresponds to a more rapid increase with change of solvent than the corresponding plot for the intercept. Further evidence for this type of correlation will be presented later.

Solvent Plasticizers.—When the pure plasticizer is itself a solvent for the polymer and if the polymer cannot be vulcanized, swelling data cannot be obtained, and alternative methods of correlation have to be devised. Purely amorphous polymers are soluble in any plasticizer, both when there is direct attraction between the long chains and the plasticizer molecules and when there is no heat effect on mixing. This last type of solvent has been called[11] an "indifferent" solvent, and the solution is the "athermal" type discussed by

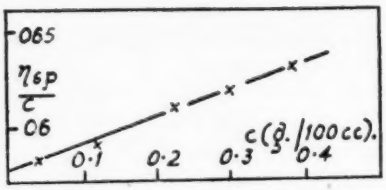

FIG. 2.—Viscosities of dilute solutions of polyvinyl acetate in ethyl acetate 25° C and 50° C.

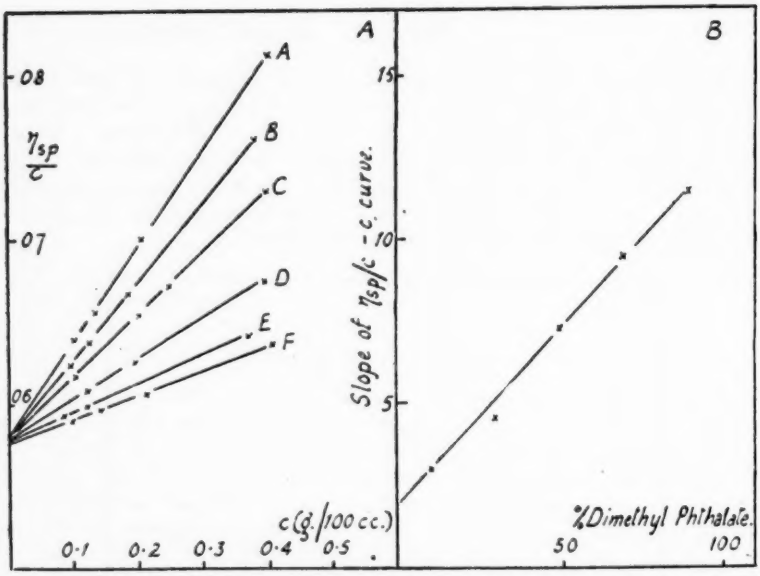

FIG. 3A.—The effect of solvent composition on the viscosity of dilute solutions of polyvinyl acetate in ethyl acetate-dimethyl phthalate mixtures 25° C. A, 90% D.M.P., 10% E.A. B, 70% D.M.P., 30% E.A. C, 50% D.M.P., 50% E.A. D, 30% D.M.P., 70% E.A. E, 10% D.M.P., 90% E.A. F, 100% E.A.

B. Relation between slope of $\eta_{sp}/c - c$ curve and solvent composition.

Hildebrand. If the relative slopes of the viscosity curves are determined by w/kT, the viscosity slopes relating to solutions formed with evolution of heat (w negative: attraction between solvent and polymer) are reduced by increasing temperature. Conversely the slopes found with solutions formed with absorption of heat are increased with temperature towards their unbiased value of a solution in an indifferent solvent. In each case the increased molecular motions at the higher temperature tend to restore the randomly kinked configuration of the polymer and, hence, the unbiased viscosity. Further, the viscosity relationships of an athermal solution will be unchanged by temperature.

A priori we should choose as a typically athermal mixture a solution of polymer in pure monomer, provided that the monomeric molecule is not unduly polar in character. In this connection the theory has been tested by an extensive study of the system ethyl acetate-polyvinyl acetate, both with and without added plasticizers. Figure 2 shows the results of viscosity experiments on dilute solutions of polyvinyl acetate in ethyl acetate alone. The straight line is the experimental curve for solution viscosities, measured at 25° C, and the dotted points the results of measurements at 50° C. There is, then, no effective variation of the specific viscosity with temperature, and we may infer that the system ethyl acetate-polyvinyl acetate is truly athermal. The effect of the composition of the mixed solvent was then studied to amplify the arguments of case (2) of the last section. Polyvinyl acetate is soluble in dimethyl phthalate-ethyl acetate mixtures over the whole range of composition, and the viscosities of the solutions in the mixed solvents are higher than those in pure ethyl acetate, indicating some degree of attraction between the polymer and the plasticizer. Figure 3A shows the curves $\eta_{sp}/c - c$ obtained in various

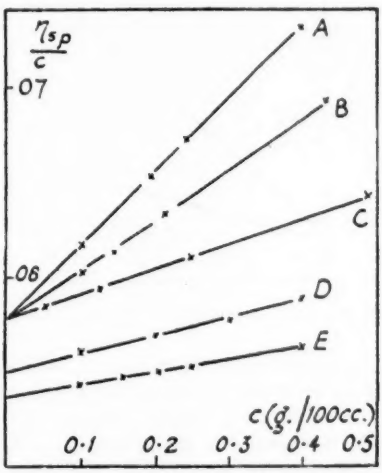

FIG. 4.—Viscosities of dilute solutions of polyvinyl acetate in 50% mixtures of alkyl phthalates and ethyl acetate. A, dimethyl phthalate 25° C; B, dimethyl phthalate 50° C; C, diethyl phthalate 25° C and 50° C; D, dibutyl phthalate 50° C; E, dibutyl phthalate 25° C.

solvent mixtures. The slopes of the curves, though not the limiting intercepts, are functions of the solvents, and in Figure 3B these slopes are plotted against the solvent composition. The relationship is quite linear as we might perhaps expect.

In so far then, as the solvents used are suitably "indifferent," the considerations given in the first half of this paper would seem to apply, and for comparative purposes we extrapolate some of these conclusions to other systems.

COMPARATIVE MEASURES OF COMPATIBILITIES

Polyvinyl Acetate.—Measurements have been made to test the relative compatibilities of a series of alkyl phthalates by measurements of the viscosities of dilute polymer solutions in 50%-by-volume mixtures of the phthalates and ethyl acetate. A solvent composition of 50% has been chosen for convenience throughout this section: it allows relatively quick solution, even in mixtures

with poor plasticizers, and the comparative effects which are observed are sufficiently marked for our purpose. The results of experiments both at 25° C and 50° C are shown in Figure 4. Solutions of polyvinyl acetate in all mixtures of ethyl acetate and diethyl phthalate have viscosities at 25° C and at 50° C, which exactly reproduce the straight line in Figure 2; the results are shown in Figure 4 as the line C. We may infer that diethyl phthalate, like ethyl acetate, mixes with polyvinyl acetate without heat change and that it is thus a good plasticizer. Dimethyl phthalate, as we have seen, appears to interact to some extent with this polymer and should show a superior compatibility. At 50° C the slope of the viscosity curve for the 50 per cent dimethyl phthalate solution is lower than the corresponding slope at 25° C; this confirms the conclusion we have just stated. As the temperature increases, the attractive forces between the plasticizer and polymer which cause the chains to uncoil slightly are increasingly compensated by the thermal agitations, and the relative viscosity

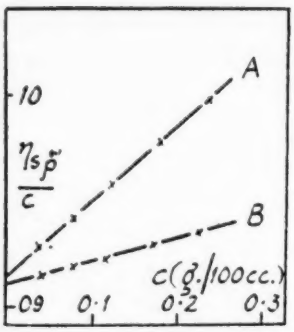

FIG. 5.—Viscosities of dilute solutions of polyvinyl chloride in cyclohexanone. A, 25° C. B, 50° C.

falls as the configurational extension becomes less. The viscosities of solutions with dibutyl phthalate and dipropyl phthalate are, on the other hand, lower than those of solutions in pure ethyl acetate, and the slopes of $\eta_{sp}/c - c$ curves are increased slightly as the temperature is raised. (The curves for dipropyl phthalate mixtures are, for clarity, omitted from Figure 4; the 25° C curve lies between the lines D and E in the figure.) We would, therefore, expect these esters to be poor plasticizers for polyvinyl acetate and to have low compatibilities. The general trend of these results is in good agreement with the known plasticizing action of the phthalate series.

Polyvinyl Chloride.—We have so far been concerned with relatively nonpolar polymers. Polyvinyl chloride is, however, essentially polar and dissolves only in polar solvents. It is extremely unlikely that such solutions are formed athermally, and many of the theoretical conditions we imposed cannot now be assumed. However, experiments show that many of the effects observed with, say, the polyvinyl acetatc systems, are found also with polyvinyl chloride solutions and, although the theoretical basis is not so clear, the experimental results, for comparative purposes, are by no means invalidated. Cyclohexanone was chosen as the most suitable solvent for the polymer, and Figure 5 shows the $\eta_{sp}/c - c$ curves for dilute polyvinyl chloride solutions in this solvent at 25° C and at 50° C. It is clear that increasing temperature decreases the η_{sp}/c values at any finite concentration, although the limiting $[\eta]$ value at zero concentration is not affected. This decreasing value of the slope

of the curves suggests that attractive forces are acting between the polymer and solvent. This means that viscosity experiments have to be made in mixed solvents which do not necessarily conform to the definition given above.

Polyvinyl chloride, however, is not soluble in the common plasticizers, and it has been possible to correlate some of the viscosity results obtained in mixed solvents with equilibrium swellings in the pure plasticizers. The viscosity results were obtained in the usual way. Figure 6 shows the $\eta_{sp}/c - c$ curves obtained for dilute solutions of the polymer in 50%-by-volume mixtures of cyclohexanone and a series of alkyl phthalates. Generally speaking the results are in good agreement with the known compatibility properties. Dimethyl phthalate is recognized as a poor plasticizer for polyvinyl chloride, and its

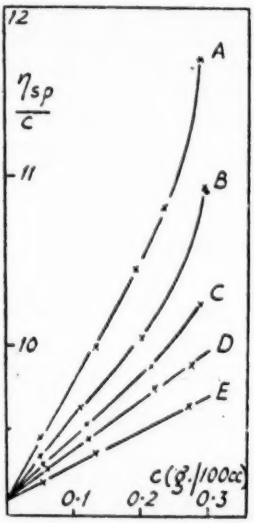

FIG. 6.—Viscosities of dilute solutions of polyvinyl chloride in 50% mixtures of cyclohexanone and alkyl phthalates, 25° C. A, dibutyl phthalate; B, dihexyl phthalate; C, dioctyl phthalate; D, diethyl phthalate; E, dimethyl phthalate.

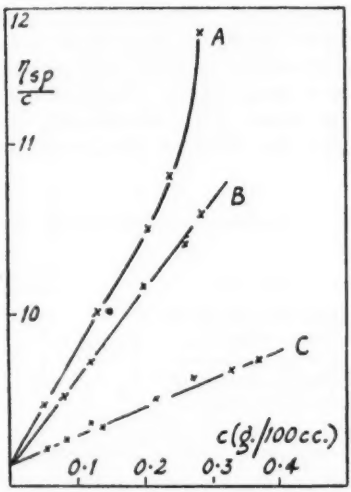

FIG. 7.—Viscosities of dilute solutions of polyvinyl chloride in 50% mixtures of cyclohexanone and alkyl phthalates. A, dibutyl phthalate, 25° C; B, dibutyl phthalate, 50° C; C, dimethyl phthalate, 25° C and 50° C.

solutions show only a very slight increase of the η_{sp}/c ratio as the concentration rises. The higher members of the series show improved plasticizing properties, and it is further recognized that some maximum of compatibility occurs at the butyl ester. Figure 7 shows the effect of temperature on the dimethyl phthalate and dibutyl phthalate systems. Although thse systems are far from the ideal ones studied in the last section, we might expect a qualitative effect of temperature on the same lines, and this is found here. The high slope of the dibutyl phthalate curve is reduced as the temperature rises: we cannot immediately say how far this effect is due to the cyclohexanone present in the mixture, but we can infer that the dibutyl phthalate either interacts directly with the polymer or has only a very small repulsive effect. The slope of the dimethyl phthalate curve is practically unchanged by temperature. Since the cyclohexanone in the solvent mixture is tending to reduce the relative viscosities at higher temperatures we must conclude that dimethyl phthalate itself is tending to repulse the polymer chains: this interaction tends to increase the relative

viscosity at higher temperatures and the net result is an apparent temperature independence of the viscosity curve. Dilute solutions of polyvinyl chloride with less than 50 per cent of dimethyl phthalate in the solvent mixture give viscosity curves whose slopes are reduced by increasing temperature.

These figures were checked further by a series of rough swelling experiments. Preliminary experiments showed that polyvinyl chloride powder is swollen by plasticizers to give homogeneous gels with supernatant clear liquids. These liquids were analyzed viscometrically and found to contain no polymer, in agreement with Bronsted's results[12] for polystyrene. Weighed quantities (0.2 gram) of the polymer were placed in small tubes and plasticizer added: the mixtures were stirred with glass rods and left in a thermostat at 25° C for a week. As much as possible of the supernatant liquid was sucked up by filter paper and the tube centrifuged at room temperature for ten minutes. The remaining liquid was then sucked up at 25° C, and the tube and gel were weighed. While readings were mutually consistent to about 3 per cent the accuracy is considerably reduced by temperature changes due to centrifuging at room temperature, excessive loss of excess plasticizer from the softer gels and in some cases semimicroscopic inhomogeneity. Consistent differences between the different plasticizers were, however, obtained, and in Table II

TABLE II

VISCOSITY AND SWELLING RELATIONSHIPS POLYVINYL CHLORIDE

Plasticizer	Q (grams of plasticizer per gram of PVC)	Slope	E_S/V_S (cal. per cc.)
Dimethyl phthalate	5.0	48	108
Diethyl phthalate	5.4	74	87
Dibutyl phthalate	6.0	174	70
Dihexyl phthalate	5.7	117	60
Dioctyl phthalate	5.3	88	60

we give figures for the phthalate series, together with estimated values of the cohesive energy density of the plasticizers and the slopes of the curves shown in Figure 6.

The equilibrium swelling appears to vary with the E_s/V_s value of the plasticizer, and there is a maximum near the butyl ester, where, presumably, the E_s/V_s value of the plasticizer is most nearly equal to the corresponding E_p/V_p ratio for the polymer. We cannot at the moment, however, carry this interpretation very far, as Gee's correlation of Q, the equilibrium swelling, and the cohesive energy density of the swelling agent applies only when heat is absorbed on mixing. Without further measurement, we cannot give a more detailed interpretation of the heat changes which occur in the complicated ternary mixtures used for the viscosity experiments. Dibutyl phthalate does not dissolve polyvinyl chloride, and we must suppose that steric or polar effects prevent complete miscibility. Such effects, of course, influence the slope of the viscosity curve, but to what extent we cannot at present say. Two points are, however, clear: the comparative slopes of the viscosity curves do represent the known series of plasticizer compatibilities, and the slopes are paralleled by the equilibrium swelling in the pure plasticizer.

Results for further series of plasticizers are given in Table III. In the phosphate series there is again known to be a maximum of compatibility at the butyl ester, and this is represented by a steep slope of the viscosity curve, and a slightly higher value of the limiting intrinsic viscosity ratio $[\eta]$, although

TABLE III

VISCOSITY RELATIONSHIPS. POLYVINYL CHLORIDE SYSTEMS

Plasticizer	Limiting value	Initial slope of viscosity curve
Trimethyl phosphate	0881	5
Triethyl phosphate	0915	113
Tributyl phosphate	0920	150
Trinonyl phosphate	0900	84
Triacetin	0805	2
Triethyl sebacate	0880	86
Tributyl sebacate	0920	176
Methyl phthalyl ethyl glycollate	0878	88
Ethyl phthalyl ethyl glycollate	0870	60
Butyl phthalyl butyl glycollate	0870	72

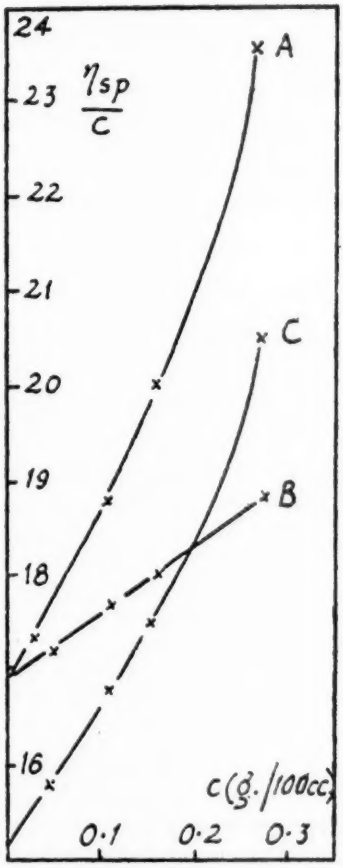

FIG. 8.—Viscosities of dilute solutions of cellulose acetate in 50% mixtures of acetone and plasticizer, 25° C. A, dimethyl phthalate; B, diethyl phthalate; C, triacetin.

this latter factor is always less affected by solvent variations than the slope of the $\eta_{sp}/c - c$ curve. The superiority of the butyl ester is shown again by comparison of the results for ethyl and butyl sebacates. Triacetin is given as an example of an extremely poor plasticizer and the phthalyl alkyl glycollate series to show a range of plasticizers of only medium efficiency.

Cellulose Acetate.—When we come to consider cellulose esters the highly polar nature of the common solvents makes any direct explanation of viscosity results rather difficult. As with polyvinyl chloride systems, however, truly comparative effects do obtain. Figure 8 shows viscosity curves for a cellulose acetate dissolved in 50%-by-volume mixtures of alkyl phthalates and acetone. Dimethyl phthalate is here shown to be rather more compatible than the corresponding ethyl ester. Dibutyl phthalate-acetone mixtures in this proportion do not dissolve cellulose acetate even in these very dilute solutions. The third curve in Figure 8 is that obtained with the same cellulose acetate in a 50 per cent mixture of acetone and triacetin: the crossing of the phthalate curves is somewhat unexpected, but the high slope shows that triacetin is an efficient plasticizer with good compatibility. If there is very strong dipole interaction, the curves obtained may be very different in nature. Thus benzene, added to a dilute solution of cellulose acetate in cresol, raises the viscosity, although it acts as a precipitant if added in sufficient quantity. Here presumably the cellulose acetate forms a compact complex with the cresol, possibly with hydrogen bonds, and this complex is broken down by benzene into the original structure of extended long chains. However, when such extreme conditions are avoided, this method of approach always gives results which are in good agreement with the plasticizing action of the liquids used, when this is known.

DISCUSSION

The experiments described here clearly lead to the following conclusions. In all the mixed solvent experiments the comparative slopes of the viscosity curves are paralleled by the equilibrium swelling in the pure plasticizer, and the slopes do represent the known series of plasticizer compatibilities. As a purely experimental method of measuring compatibilities viscosity measurements of this type seem very satisfactory. It remains to see how far the experimental results are in quantitative agreement with any theoretical predictions. The theory previously developed[9] to account for solvent effects basically assumed that the value of η_{sp}/c at zero concentration was proportional to the mean square length of the molecule, according to calculations of Huggins[13] and Kuhn[14]. Finite values of w, the interaction between polymer and solvent, alter the value of $\overline{L^2}$ in such a way that $\overline{L^2} = (1 + a')\overline{L_0^2}$ where a' depends both on w and on the concentration c. In the limit of zero concentration, and of course when there are no heat effects, a' tends to zero. No further specific account was taken of the possible effects on the viscosity of increasing interaction between chains. The final equation derived for η_{sp}/c was written:

$$\frac{\eta_{sp}}{c} = A + \left\{ B' - \frac{Bw}{\boldsymbol{kT}} \right\} \cdot c$$

so the slope of the $\eta_{sp}/c - c$ curve should be a linear function of $w/\boldsymbol{kT}$. In mixed solvents of the type defined and considered here, η_{sp}/c can be similarly calculated as a linear function of $w/\boldsymbol{kT}$, where w is the single interaction between the polymer and plasticizer S_2: η_{sp}/c should also be a linear function

of the volume fraction of liquid S_2 in the solvent mixture. An obvious experimental check on the validity of these assumptions would be to measure directly ΔH, the heat of mixing of the polymer and plasticizer. The direct calorimetric measurement of ΔH is not easy, and indirect measurements have to be devised which are experimentally more feasible. Gee and Treloar[4] showed that the heat of mixing of rubber and benzene was nearly equal to that of benzene and a simple hydrocarbon. This suggests that calorimetric measurements with systems of plasticizer and monomer should give ΔH values closely related to the interaction between the plasticizer and the polymer link. Experiments on these lines are at present being carried out by P. Meares in this laboratory. Unpublished results on ethyl acetate-alkyl phthalate systems confirm the interpretations placed on the viscosity results shown here in Figures 2 to 4. This agreement and the good correlations found with swelling data clearly show that there is a close connection between the slopes of the viscosity curves and the polymer solvent interactions. The exact form of this relationship is, however, not yet experimentally proved.

Further quantitative agreement with the theory is not obtained. The effect of solvent is essentially one of the second order. The viscosity ratio η_{sp}/c increases with concentration in any solvent due to increasing interference between the chains, so the B' term in the equation for η_{sp}/c is large and positive and to a first approximation independent of temperature. The Bw/kT term is something like a correcting factor. Since $1/T$ varies only slightly in the range 25° C–50° C, the effect of temperature on the slope of the curve should be very small, and probably within the experimental error. The large variations which are obtained experimentally contradict this, and the disagreement is serious. Qualitatively the predicted effect of temperature is in the right direction; as the temperature rises, the molecular movements become increasingly strong, the random configurations of the chains become more probable, and the unbiased viscosity is favored. The reasons for this failure to account exactly for the experimental results must be due to the crudeness of the underlying assumptions. In the original theory the use of Huggins' equation, assuming proportionality between η_{sp}/c and $\overline{L^2}$, is valid only in the limit of zero concentration. As the concentration increases this relationship ceases to hold exactly, and the theory obviously did not take sufficient account of the increasing resistance to flow caused by increased contacts between chains. As the concentration increases then, interference between the chains accentuates and eventually overmasks the small effects originally considered. As the chains uncoil in a "good" solvent, there are of course increased contacts between separate chains, and the slope of the viscosity curve is high. Qualitatively the suggested solvent effects account for the experimental results, but a quantitative relationship between the polymer-solvent interaction and the slope of the viscosity curves, although demonstrated experimentally, remains theoretically unproved.

SUMMARY

The general problem of plasticizer compatibility is discussed, and it is suggested that a comparative measure of compatibility can be obtained from experiments which measure polymer-plasticizer interactions (w). Experiments are described which measure the viscosity of dilute polymer solutions in suitable mixed solvents containing the plasticizer in question. The slope of the $\eta_{sp}/c - c$ curve is shown to be related to the equilibrium extent of swelling

of the polymer in the pure plasticizer and, in general, the slope of the curve is a good comparative measure of the plasticizer's compatibility. The effects of temperature and composition of the mixed solvent are also discussed. The experiments are considered in the light of a previous theory of the effect of solvent on the η_{sp}/c ratio: the results do not support the suggested view that the slope of the $\eta_{sp}/c - c$ curve is a simple linear function of w/kT.

ACKNOWLEDGMENT

My thanks are due to the Geigy Colour Company, and to Boake, Roberts & Co., Ltd. for the supply of materials. I should like to express my thanks to Professor E. K. Rideal for much encouragement and advice and also to G. Gee for his help in the presentation of this paper.

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RISE OF TEMPERATURE ON FAST STRETCHING OF BUTYL RUBBER *

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INTRODUCTION

The rise of temperature on fast stretching is one of the noteworthy characteristics of rubber stocks. If one stretches rapidly a Hevea gum band several hundred per cent and applies it to the chin, one gets a direct sensory observation of the heat developed. This shows that the temperature must have been higher than that of the body, *i.e.*, there must have been a temperature rise of 12–15° C. Surprisingly enough such a "high heat" was not observed when the human lip was replaced by a supposedly more objective apparatus, namely, by a thermocouple in conjunction with a galvanometer. In addition, different authors reported different values for the heat rise—all much lower than 15° C. Recent work in this laboratory by Dart, Anthony, and Guth[1] was done with a fast galvanometer. This work showed that the use of slow galvanometers was one reason why previous investigators could not observe "high heat". In addition, a survey of various types of natural and synthetic gum and tread stocks showed that the heat generated depends on the type of stock used. This accounts for the disagreement among earlier investigators.

The work of Dart, Anthony, and Guth[1] showed that, for gum stocks, rise in temperature on extension is a slowly rising function of the extension. This slow rise is attributable to the heat into which the work of stretching is transformed. For stocks which crystallize on stretching, the rise in temperature takes a steep upward turn and continues almost linearly after the onset of crystallization. This was found to be the case for Hevea and Neoprene. Hycar-OR, on the other hand, did not show the upward turn in agreement with x-ray data, which do not reveal any crystallization for this type of synthetic. Now, for the case of Butyl gum stocks, x-ray data show that they do crystallize on stretching, but start only at very high extensions (500 per cent and higher). Therefore it seemed to be of interest to study the onset and continuation of crystallization for Butyl stocks by means of "high heat" curves.

In addition the initial cooling effect at small extensions was studied by employing a sensitive but slower galvanometer. Changes of temperature as small as 0.001° C ("low heat") could be observed. The experimental technique for taking both high and low heat data was greatly improved and simplified compared to our earlier work[1]. Moreover, besides taking extension and delayed retraction curves[1], the residual heat for extension and immediate retraction (fast cycle) was observed.

* Reprinted from *The Journal of Chemical Physics*, Vol. 13, No. 1, pages 28–36, January 1945. This paper was presented at the Inaugural Meeting of the Division of High-Polymer Physics of the American Physical Society, Rochester, N. Y., June 23, 1944.

EXPERIMENTAL METHOD

A compressed-air driven machine was used to obtain rapid extensions and retractions. With this machine, extensions can be produced from 0 per cent up to any elongation in 0.1 second. The machine can also be used for rapid extension-retraction oscillations up to frequencies as high as 600 per minute, and the gradual rise of temperature in the sample can be followed as a function of number of cycles, speed of cycles, and degree of elongation.

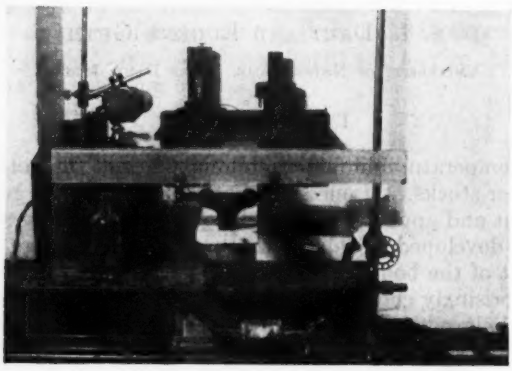

FIG. 1.

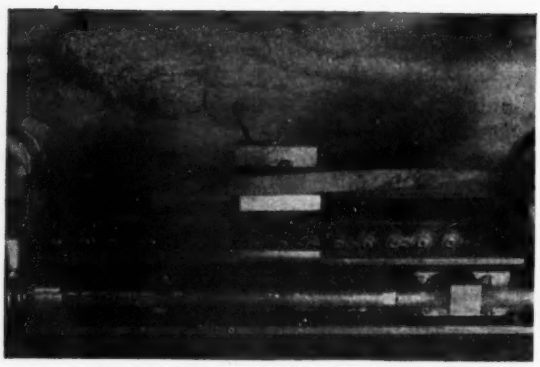

FIG. 2.

Temperatures were measured with a copper-constantan thermocouple sandwiched between two samples given a half-twist. For small temperature changes a galvanometer of longer period, about 8 seconds, and a sensitivity of 4×10^{-9} ampere per millimeter was employed. This apparatus is shown in Figures 1 and 2.

COMPOSITION OF THE STOCKS

The stocks were prepared for us by the Esso Laboratories. The ingredients of each vulcanizate are given in parts by weight in Table I. Numbers 1, 2, 4, and 5 were cured for 60 minutes at 307° F; number 3 (nonsulfur cure) for 45

minutes at 287° F. Slabs with dimensions 13.5 × 13.5 × 0.25 were cured for 70 minutes.

TABLE I

Stock No.	1	2	3	4	5
Butyl-A	100	100	—	—	—
Butyl-B	—	—	—	100	100
Zinc oxide	5	5	—	5	5
Stearic acid	3	3	—	3	3
Sulfur	1.5	1.5	—	1.5	1.5
Calbot No. 9 Black	—	50	—	—	50
Tetramethylthiuram disulfide	1	1	—	1	1
Mercaptobenzothiazole	—	0.5	—	—	0.5

PHYSICAL PROPERTIES OF THE RAW STOCKS AND TENSILE DATA FOR THE CURED STOCKS

The following data were communicated to us from the Esso Laboratories.

The Butyl-A raw stock possessed about 0.95 mole per cent (based on the C_4H_8 chain unit) of unsaturation according to the Kemp-Wijs method, the unsaturation figure for the Butyl-B polymer is about 1.5 per cent. Their intrinsic viscosities are about the same, 1.25 in diisobutylene at 20° C. The corresponding viscosity average molecular weight is 290,000.

Tensile data for the cured stocks are given in Table II.

TABLE II

Stock	Load at 300% lb./in.²	T.S. lb./in.²	B.E. in %
1	—	1900	950
2	280	2500	790
3	950	2000	500
4	—	2900	1000
5	380	2675	780

RESULTS ON HIGH AND LOW HEAT

High heat curves for stocks 1–5 are given in Figures 3–7. All three curves (extension, retraction, fast cycle) were obtained using one single sample.

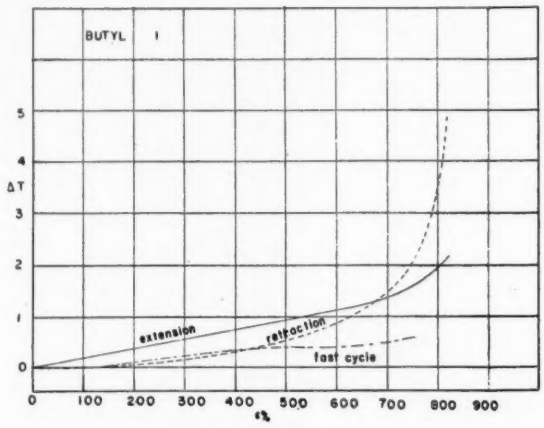

FIG. 3.

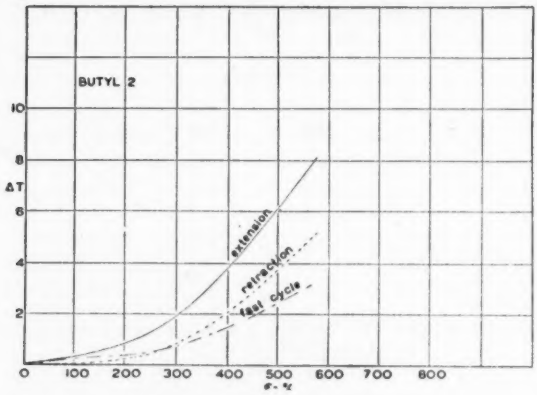

FIG. 4.

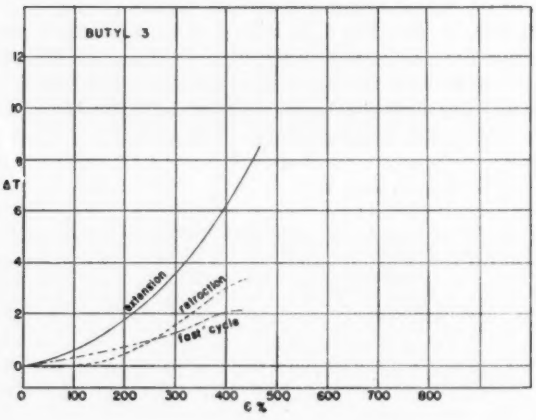

FIG. 5.

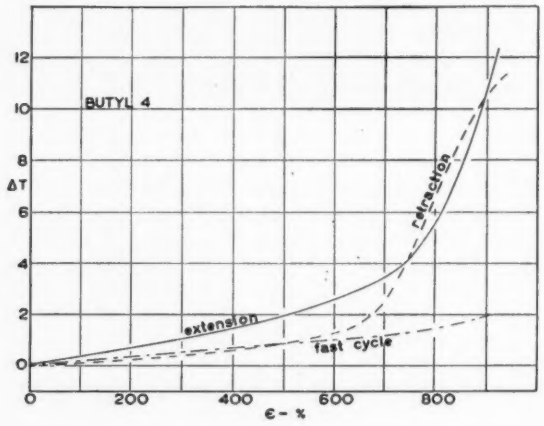

FIG. 6.

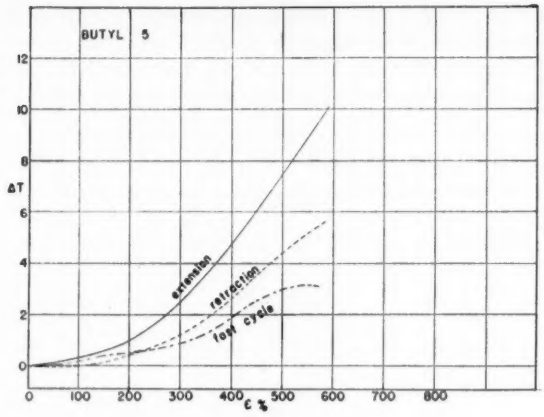

FIG. 7.

Previous work in this laboratory[1] has shown that somewhat higher ΔT values can be obtained by using a different sample for each extension, the reason being that some temporary or permanent set was introduced at each extension. However, variations within the batch partially offset this advantage of using different samples. The ΔT values obtained give the curve denoted "extension". After the sample had been stretched (in about one-tenth of a second), it was kept extended for one minute and then the machine pushed it back (again in one-tenth of a second) to the unstretched state. The negative of the temperature change involved in this (forced) retraction process is plotted as "retraction". The curve designated "fast cycle" represents the residual ΔT value for an extension and immediate (forced) retraction. Again, extension and retraction took place in two tenths of a second.

Low heat curves for stocks 4 and 5 are given in Figures 8 and 9. Extension, retraction, and fast cycle curves were obtained in the same way as for the case of high heat.

DISCUSSION OF THE RESULTS

The first question we have to answer is that concerning the basic physical significance of the extension, retraction, and fast cycle curves.

EXTENSION CURVES

Thermodynamics (Kelvin, 1855) gives the formula for the change of temperature ΔT on adiabatic extension:

$$\Delta T = \frac{T}{C_L} \int_1^L \left(\frac{\partial Z}{\partial T} \right)_L dL \tag{1}$$

where T is the absolute temperature, C_L the specific heat at constant length per cc. (independent of L), L the relative length (extended length divided by original length, the original length taken at the initial temperature T), Z the stress (actual force per unit original cross section).

$$L = (\epsilon/100) + 1 \tag{2}$$

expresses L in terms of the more familiar percentage extension ϵ. Formula (1) correlates the temperature coefficient of the stress at constant extension $(\partial Z/\partial T)_L$ with the change in heat $\Delta T \cdot C_L$ on adiabatic stretching. The change (rise) in temperature on adiabatic stretching is entirely similar to the

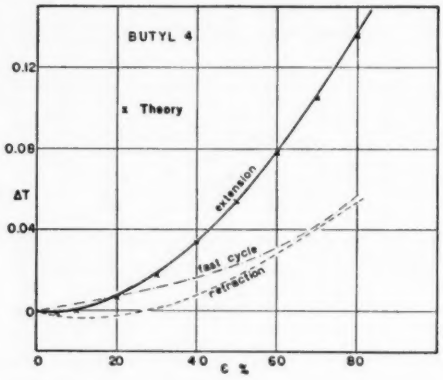

FIG. 8.

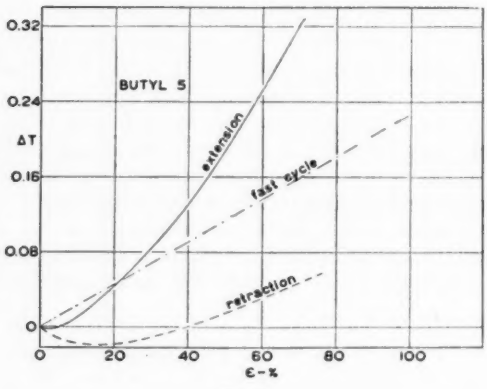

FIG. 9.

rise in temperature on adiabatic compression of a gas. The physical meaning of Equation (1) is clearer if we recognize that, as shown by Anthony, Caston, and Guth[2] and by James and Guth[3]:

$$T(\partial Z/\partial T)_L = T(\partial S/\partial L)_T = Z_{(S)} \tag{3}$$

S is the entropy as a function of L and T, and $Z_{(S)}$ designates the entropy part of the stress. Then:

$$\Delta T = \frac{T}{C_L}\int_1^L Z_{(S)}dL \tag{4}$$

or

$$(d/dL)(C_L\Delta T) = Z_{(S)} \tag{4'}$$

i.e., differentiation of the ΔT *vs.* L curve yields $Z_{(S)}$ if C_L is known. If C_L is not known, (4') still yields $Z_{(S)}$ except for the numerical factor C_L.

The foregoing makes clear the physical significance of the ΔT *vs.* L curves for extension. Formula (4) is established first for a single phase. If a (more or less slow) crystallization process occurs in a certain L range, Equation (4) holds also through crystallization.

The general behavior of $Z_{(S)}$ is already known from the work of Anthony, Caston and Guth[2] and James and Guth[3]. There a relaxation method[2] was applied to obtain $Z_{(S)}$. The range of crystallization was investigated by Wiegand and Snyder[4], Meyer and Ferri[5], Caston, Anthony, and Guth[6] and recently, more accurately by Wood and Roth[7]. From these investigations, it follows that the $Z_{(S)}$ *vs.* L curve looks schematically as drawn in Figure 10.

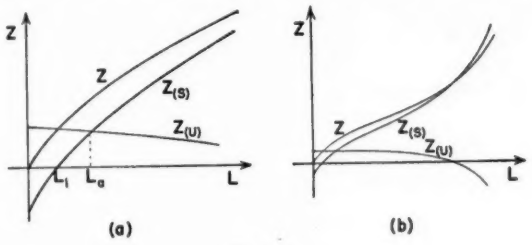

FIG. 10.

(a) is drawn to a larger scale than (b) to show clearly the thermoelastic inversion. Here we plotted, besides $Z_{(S)}$, the total stress Z and the internal energy component:

$$Z_{(U)} = Z - Z_{(S)} \tag{5}$$

The integral of $Z_{(S)}$ as derived from Figure 10 appears as shown in Figure 11 (assuming $C_L \leqq 0.4$), *i.e.*, the change in temperature is first negative, passes

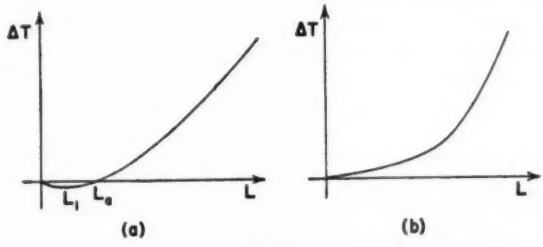

FIG. 11.

through a minimum, given by $(\partial Z/\partial T)_L = 0$, goes to zero and becomes positive.

$$(\partial Z/\partial T)_L = 0 \tag{6}$$

defines the isometric (= isotonic) thermoelastic inversion point because, at the extension L_i, given by the root of (6), the sign of the slope of the isometrics (Z-T curves at constant L) changes.

$$\Delta T = 0 \tag{7}$$

defines the adiabatic thermoelastic inversion point, L_a. Both L_i and L_a are indicated in Figure 10(a).

The statistical theory of James and Guth[8] gives an expression for $(\partial Z/\partial T)_L$ which contains only one adjustable parameter K and the measurable cubic thermal expansion coefficient α of the unstretched sample (T_0: room temperature 300° K):

$$\left(\frac{\partial Z}{\partial T}\right)_L = K\left[L - \frac{1 + \alpha T_0}{L^2}\right] \tag{8}$$

valid for the range of extension of Figures 10(a) and 11(a). Inserting into (1) we obtain:

$$\Delta T = (KT/2C_L)[L^2 + L - 2(1 + \alpha T_0)] \times [(L - 1)/L] \tag{9}$$

From (8) and (6) we have:

$$L_i = 1 + (\alpha/3)T_0 \tag{10}$$

from (9) and (7) it follows that:

$$L_{ad} = 1 + (2\alpha/3)T_0 \tag{11}$$

We have measured α both for the gum and the tread stock and obtained:

$$\alpha\text{-gum} = 1.74 \times 10^{-4} \tag{12}$$

$$\alpha\text{-tread} = 1.17 \times 10^{-4} \tag{13}$$

The value of α-gum looked somewhat low in view of the fact that for many Hevea and synthetic gum stocks $\alpha \cong 2.1 \times 10^{-4}$. However, a glance at Figure 8 shows that experimentally:

$$\begin{aligned} L_i &= 1.05 \\ L_a &= 1.10 \end{aligned} \tag{14}$$

which are just exactly the theoretical values according to (10) and (11) if we substitute (12). The crosses in Figure 8 indicate the theoretical values for ΔT using again (12). The agreement with experiment is rather good.

For extensions up to 700 per cent, the ΔT *vs.* L curves rise slowly. This whole range is covered by the statistical theory of James and Guth[3]; we only have to replace (8) by its generalization involving the inverse Langevin function.

Physically, in this range 0–700 per cent the work done on stretching transforms practically completely into heat, $C_L \cdot \Delta T$.

For extensions above 700 per cent, however, crystallization sets in. The $C_L \cdot \Delta T$ corresponding to the steep upward turn of the high heat curve represents the latent heat of crystallization. The above interpretation holds for gum stocks, *i.e.*, Figures 3 and 6. The tread stocks, Figures 4 and 7 and the nonsulfur cure, Figure 5, show different behavior. Here the high-heat curve starts its upward turn much earlier. The early upward turn for tread stocks is partly attributable to an earlier onset of crystallization as a consequence of carbon black reinforcement. Partly, however, it is due to frictional heat between the rubber matrix and carbon black.

This interpretation for gum stocks is supported by considering the retraction curve.

RETRACTION

The retraction curve is more arbitrary than the extension curve, since the one-minute delay could be replaced by a shorter or longer waiting period,

thereby changing the retraction curve. Below the range of crystallization the retraction curve is always below the extension curve, in accordance with the second law of thermodynamics.

At the onset of crystallization the retraction curve crosses the extension curve, owing to the fact that additional crystallization takes place during the waiting time of one minute. It was shown[1] that the crystallization process takes time. After completion of crystallization, we have again one phase, and retraction recrosses the extension and is again below it. This may be seen in Figure 6.

An estimate of the latent heat of crystallization may be obtained by taking the difference in ΔT between the two crossings. The difference in ΔT between the two crossings, multiplied by C_L, measures the heat of crystallization. We see from the steepness of rise of the extension and retraction curves that the heat of fusion is very considerable (cf. Figure 6).

FAST CYCLE CURVES

These curves give actually the hysteresis loop between the extension and retraction branch of stress-strain curves taken in 0.2 second. For, that loop is simply given by:

$$\text{Loop} = C_L \cdot \Delta T \tag{15}$$

This loop (of Figure 12) corresponds to the dynamic hysteresis loop for extensional free or forced vibrations around a static strain of $\epsilon^*/2$ and with a constant dynamic amplitude of $\epsilon^*/2$, and a frequency of 5 cycles per second. It

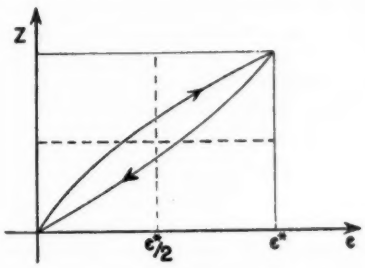

FIG. 12.

does correspond more closely to the first cycle of a free or a forced vibration. A comparison with sustained forced vibrations is possible, of course, by observing ΔT for repeated fast cycles. The relation of the fast cycle curves to rebound data is the same as that of the corresponding free vibrations. Of course, the static strains and amplitudes employed in forced or free vibrations are of the order of 10–30 per cent, whereas the amplitudes for high heat measurements may go right up to the breaking elongation, *i.e.*, up to 1000 per cent.

It should be pointed out that the impact resilience as measured by the rebound of a ball or of a pendulum depends both on the dynamic hysteresis loop and upon the dynamic modulus, *i.e.*, stiffness of the stock. Roughly, we may consider the rebound as a half free vibration. For the percentage resilience R we obtain then:

$$R = (h_R/h) = \exp(-H_A/A^2E)$$

where h_R is the height of rebound, h is the height of fall, H_A is the energy loss per cycle for vibrations with constant amplitude A, and E is the dynamic modulus[9].

We wish to point out that the hysteresis loops corresponding to fast cycles (0.2 second) are presumable solely or mostly due to internal friction.

"Static" hysteresis loops, obtained with comparatively slow-speed stretching (for instance, with the usual 20 inches per minute), are due to stress relaxation. There is a correlation between the two types of hysteresis loops, but probably not a simple one. We shall discuss this correlation in another place.

The fast cycle curves are not the difference between extension and retraction. Particularly for the gum stocks the fast cycle curves increase much slower with the elongation than the extension and retraction curves. For small elongations, Figure 8 shows the fast cycle to rise almost linearly in the beginning and then approach the retraction branch.

GENERAL DISCUSSION

GUM STOCKS

Low Heat

The low heat curve for Butyl gum (Compound 4) may be compared with that of a Hevea gum, cf. Figure 5 of James and Guth[3]. The extension curves are about the same for Butyl and for Hevea. Since Butyl at the same elongation has a lower stress value than Hevea, *i.e.*, the value of K is smaller for the former, the value of C_L must also be smaller for Butyl than for Hevea. This conclusion will be checked by direct measurement of C_L. The smaller value of the thermal expansion coefficient also tends to raise ΔT, but this influence acts only in the neighborhood of the thermoelastic inversion point.

The retraction and fast cycle curves (the last not given in Figure 5 of James and Guth[3]) differ greatly for Hevea and Butyl. Since Butyl shows less stress relaxation than Hevea, this difference must be due to the considerably greater internal friction of Butyl.

High Heat

The extension curves for stocks in Figures 3 and 6 have roughly the same form up to about 400 per cent. It should be pointed out that the accuracy of high-heat curves increases with the elongation because of the better contact between the rubber and the thermocouple. Above 400 per cent the curve rises faster for Stock 4 than for Stock 1. This behavior is in keeping with the higher tensile strength and somewhat higher breaking elongation of Stock 4 in contrast to Stock 1. It is to be expected that between 800 and 1000 per cent a further steep rise of ΔT occurs, in view of the steep rise of the stress-strain curves in this region. Experiments are underway to check this conclusion.

The retraction curves coincide for the two stocks up to about 600 per cent elongation. From there on the curve for Stock 4 rises steeper than that for Stock 1.

The fast cycle curves rise very slowly for both stocks. The investigation of the range above 800 per cent will be interesting.

Comparison of the Butyl high heat curves of Figures 3 and 6, with the high heat curve of a Hevea gum stock (cf. Figure 4 of Dart, Anthony, and Guth[1]) is quite revealing. That particular Hevea gum stock crystallizes at about 250 per cent elongation, as the first crossing of the extension and retraction

curves indicates. Actually the retraction branch is somewhat lower than the extension branch below 250 per cent, as more accurate experiments have shown. However, the difference between extension and retraction is smaller for Hevea than for Butyl. The characteristic difference between Hevea and Butyl is, of course, the late and more abrupt crystallization of Butyl in contrast to the earlier and more gradual crystallization of Hevea. This is indicated in the schematic Figure 13 where the solid curve represents extension and the dashed curve retraction. The first crossing indicates the onset of crystallization.

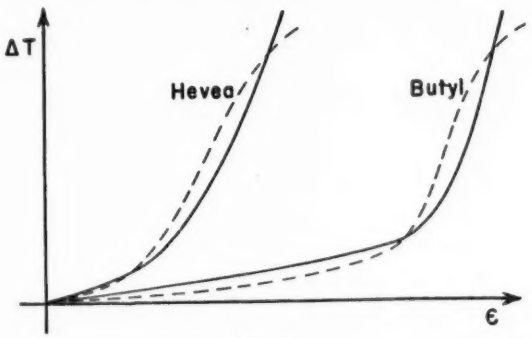

FIG. 13.

The correlation of stress-strain curves (and hysteresis loops) with x-ray data is somewhat complicated by the fact that x-ray diagrams are taken over a period of hours during which the rubber samples are kept at constant extension and suffer stress relaxation. No such difficulty enters into the discussion of crystallization based on high heat data. As a matter of fact, high heat data may be helpful in establishing the correct relationship between x-ray and stress-strain data.

TREAD STOCKS[10]

Low Heat

Figure 9 for stock 5 shows a thermoelastic inversion point and a much steeper rise of the low heat curve than Figure 8 for the gum stocks. This steeper rise is, of course, caused by the stiffening of the stock by carbon black reënforcement. The difference between the extension and retraction branches is also much bigger for the tread than for the gum stocks. The Butyl tread shows a low heat curve essentially similar to the Hevea tread, the separation between extension and retraction branches being larger for Butyl than for Hevea.

High Heat

Figures 4 and 7 show the data for the stocks 2 and 5, respectively. Figure 5, the nonsulfur cure, shows essentially the behavior of a very stiff tread stock. For tread stocks, the retraction branch is always below the extension branch, without any crossing. Conclusions about the onset of crystallization may be drawn only from the steepness of the curves. Therefrom one would conclude that crystallization starts between 200 and 300 per cent. Figure 14 compares high-heat curves for Hevea and Butyl tread. The cross on the

curves indicates the onset of crystallization. The Hevea curve is taken from Figure 7 of Dart, Anthony, and Guth[1]. Comparison of Figures 13 and 14 shows that the carbon black induces an earlier crystallization, both in Hevea and in Butyl. Consequently stronger forces act between the chains of a tread than for a gum stock. To get a correct view of carbon black reënforcement in Butyl rubber, it seems necessary to consider the whole stress-strain curve and

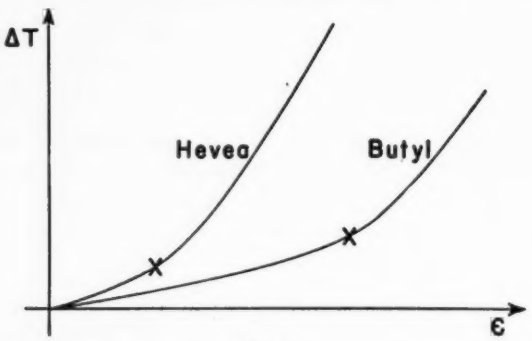

FIG. 14.

the whole high-heat curve, not just tensile strength. It has been pointed out already by Turner, Haworth, Smith, and Zapp[11] that, on the basis of tensile strength alone, carbon blacks do not reënforce Butyl, but they enhance other physical properties, as for instance, modulus and tear resistance. Figure 15 shows the stress-strain curves for Stocks 4 and 5.

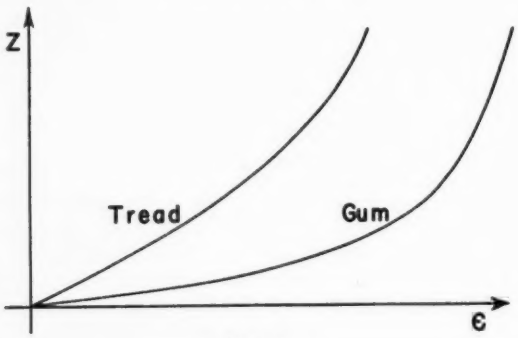

FIG. 15.

One sees that, in the range 0–750 per cent, a reënforcement of the same degree takes place as for GR-S; actually, it is smaller for Butyl than for GR-S. This range is characterized by the absence of crystallization. It seems that a certain irregularity, suppressible by crystallization, is necessary for a specifically large reënforcement by carbon black. The fact that Butyl gum does crystallize appreciably beyond 750 per cent, as evidenced by the abrupt rise in the high-heat curve and in the stress-strain curve itself, does not count, so to speak, since the black stock breaks at 780 per cent. In Hevea, blacks also cause a decrease in the breaking elongation, but since crystallization is more gradual, crystallization and carbon black add up, roughly speaking, in the reënforce-

ment. Now for Hevea, the reënforcing effect is relatively larger for an undercure than for the optimum cure (determined by maximum tensile), and relatively smaller for an overcure. The probable reason is that for an undercure the breaking elongation is higher, and so crystallization and carbon black have a larger region to add up for reënforcement. From this point of view, it would be interesting to see how far an undercured Butyl stock may be reënforced by blacks. Although the undercured Butyl gum has a lower tensile than the optimally cured, the corresponding black stocks may reverse in the order, particularly, if the breaking elongation of the black stock could be extended, say over 900 per cent. It should be pointed out, however, that the work of Turner, Haworth, Smith, and Zapp[11] (cf. their Figures 5 and 6) does not indicate such a reversal.

Another possible way of obtaining higher black tensiles would be a shift of the range of crystallization to lower extensions or to make it start earlier so that it would be more gradual and less abrupt[12]. The experimental methods described in this paper could be very helpful in such attempts to improve Butyl.

CONCLUSIONS

Study of the rise in temperature by fast stretching of Butyl gum and tread stocks throws considerable light on crystallization, internal friction, and carbon black reënforcement as functions of elongation and other possible variables. For low elongations, the low-heat curves show the occurrence of thermoelastic inversion. They show also that internal friction is much larger in Butyl than in Hevea. For high elongations the high-heat curves enable one to follow the late and abrupt crystallization so characteristic for Butyl stocks. The carbon black reënforcement of Butyl is followed for the whole range of elongations up to the breaking point. Specific carbon-black reënforcement takes place in the range of elongations before crystallization of the gum stock, but the shortening of the breaking elongation by the black excludes to a large extent the added reënforcement through crystallization.

Physical measurements of the type reported in this paper serve a manifold purpose. They enable one to establish a correlation between physical properties and chemical structure. Such a correlation is simpler for fundamental physical properties, as the ΔT *vs.* ϵ curve, than for more complicated physical tests, as data from flexometer, which were designed to approach service conditions. Comparing different gum stocks with Butyl polymers among themselves and with Hevea or other synthetics, these measurements may guide the development of better Butyl polymers. Finally, comparing tread with gum stocks, they may help to recognize the nature of reënforcing by carbon blacks and the action of other compounding ingredients.

ACKNOWLEDGMENT

The authors wish to express their indebtedness to J. P. Haworth, John Rehner, Jr., and P. J. Flory of Esso Laboratories for the preparation of the samples used in this study, for the physical test data, and for valuable discussions on Butyl rubber.

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THE ROLE OF OXYGEN IN THE PLASTICIZATION OF RUBBER *

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The close relation between the degree of mastication of raw rubber and the plasticity of the milled rubber (or the viscosity of its solutions) has been practical knowledge since the earliest days of rubber manufacture. The first definite evidence of the possible importance of atmospheric oxygen in the plasticization of rubber dates apparently to the early days of the Research Association of British Rubber and Tyre Manufacturers[1].

The final Summary in its second Research Report[2] in 1921 contained the following statements:

"Raw rubber may be heated in an atmosphere of steam, hydrogen or nitrogen to a temperature of 150° C without any very great change being brought about in its solution viscosity."

"The effect produced by milling can be imitated by heating rubber in the presence of oxygen or air."

"The marked changes in solution viscosity which are produced in rubber by heating in air are due to some chemical action between the rubber and the oxygen present."

The report ended: "It is scarcely necessary to point out the importance of the above observations in connection with the changes which occur during washing, drying (both in air and in vacuo) in the milling of raw rubber and in connection with the storage of unvulcanized compounded stock."

The similarity of the course of the viscosity alteration (of 2 per cent solutions in benzene) with progressive heating at 137° C and 150° C with access of air and progressive factory milling is shown by Figure 1, based on results given in this Report. The viscosity figure (2760) for rubber heated for 4 hours at 150° C, with exclusion of air lies outside the range of the diagram.

Although this appears to have been the first clear recognition of the direct effect of atmospheric oxygen, the empirical application of the effect goes back to the early days of rubber manufacture. In his Personal Narrative[3] Thomas Hancock, describing the development of his manufacturing procedure at about the year 1820 states: "When it became necessary, as it soon did, to hasten the production, it was found of great advantage to expose the rubber before it entered the machine[4] to as high a temperature as could be safely adopted. . . . I had a brick oven built and employed a regular baker to attend it. The rubber was placed in earthen pans, and he was directed to make the rubber as hot as possible without melting it. This mode of heating was followed until, in 1822, I began to heat the rubber in metal vessels surrounded by high pressure steam."

This principle was also invoked by Worthington and Hyde[5] who described the heating of raw rubber in steam for a similar purpose. The steam (and

* Reprinted from the *India-Rubber Journal*, Vol. 108, No. 26, pages 731–732, 734–735, June 30, 1945; Vol. 109, No. 1, 14–15, July 7, 1945.

rubber) doubtless retained some free oxygen. Later a method was described[6] for the production of softened or plasticized rubber by heating under deliberately oxidizing conditions, *e.g.*, in air at 165–175° C until an increase in weight of at least 0.5 per cent is obtained. This figure if intended to refer to oxygen absorbed, is probably excessive.

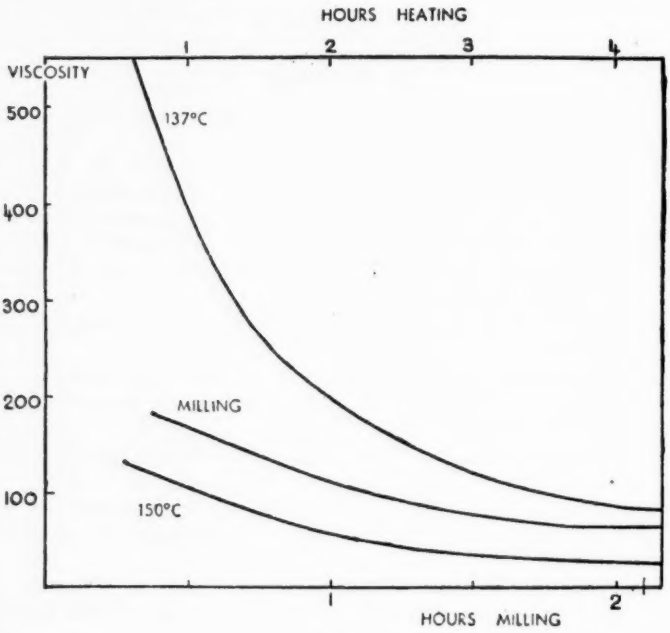


FIG. 1

In 1931, however, the position generally was much clarified when Cotton[7] in this country and shortly afterwards Busse[8] showed that access of oxygen or air is essential to the breakdown or plasticization of rubber in the customary milling or masticating operation. During such milling in air, moreover, careful observation reveals an increase in weight. The softening by milling is to be attributed therefore to the breaking up of long molecules into shorter ones by an oxidation process. The term "depolymerization" and "disaggregation", which had previously been used in a loose sense as alternative terms for "plasticization", became to that extent justified.

SOLUBILITY OF OXYGEN IN RUBBER

As plasticization therefore involves chemical oxidation of rubber molecules, it is reasonable to assume that oxygen must first pass into solution in the rubber and that its solubility and diffusion in the rubber must be important factors in plasticization, whether a static heating or the milling process is under consideration.

The solubility of oxygen in natural rubber is greater than in GR-S; the following figures[9] are for 40° C.

Natural rubber 17.8×10^{-5} g. per g. of rubber per atmosphere; approx. 13 per cent by volume.

GR-S 12.5×10^{-5} g. per g. of rubber per atmosphere; approx. 7.5 per cent by volume.

The permeability also of natural rubber to oxygen and other gases is greater than that of the commoner synthetic rubbers, such as the Bunas[10].

It would be expected, therefore, *ceteris paribus*, that natural rubber would lend itself more readily to plasticization by processes involving the effect of oxygen, *e.g.*, by milling or by thermal processes in air. Other factors, however, are not equal and weigh still more heavily in favor of plasticization with natural rubber. With GR-S and Buna-S the tendency to cross-linkage or cyclization is opposed to ease of plasticization, both in the raw material and in the vulcanized scrap. The standardized presence of added antioxidant in raw GR-S or Buna-S does not appear to be a seriously adverse factor; the ratio of the rate of chemical absorption of oxygen to the amount of dissolved gas, for GR-S at least, is approximately equal to the corresponding ratio for natural rubber.

The above solubility figures permit interesting, although rough, calculations. In aging experiments with vulcanized natural rubber in air between

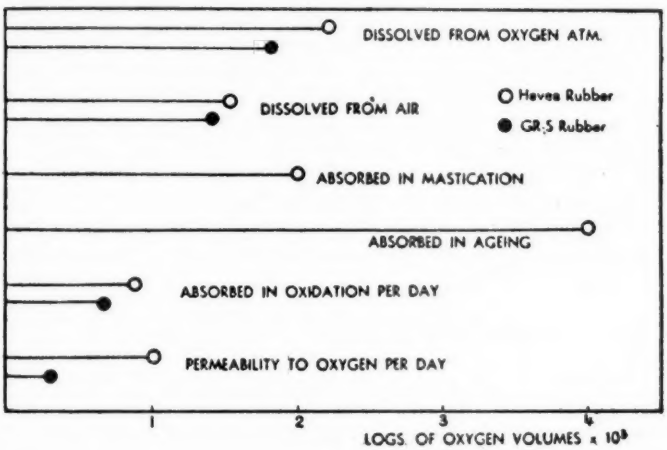


FIG. 2

13° and 70° C, it has been shown[11] that a 50 per cent loss in tensile strength is accompanied by combination with roughly 1 per cent by weight of oxygen, *i.e.*, with approximately 200 times the quantity of oxygen which the rubber could dissolve up to saturation under atmospheric pressure, and roughly 1,000 times the quantity which it would dissolve from air. These figures incidentally indicate some of the difficulties in the satisfactory artificial acceleration of aging of rubber because increase of temperature increases the rate of the chemical oxidation process so greatly that it becomes difficult or impossible to maintain an adequate renewal of dissolved gas for uniform continuance of the process, even by considerable increase in the oxygen pressure[12].

Similarly making, from viscosity measurements, the reasonable assumption that normal milling involves an approximately 50 per cent decrease in the average molecular weight of the rubber, a proportion of one molecule of oxygen per molecule of rubber of average molecular weight 300,000 would involve chemical absorption of approximately 0.01 per cent by weight of oxygen. This

proportion is much greater than could be dissolved from air at normal atmospheric pressure by the rubber even at 40° C. The logarithms of the relative magnitudes are roughly indicated in Figure 2.

The milling process among its several advantages (see later), by continuous exposure of fresh surfaces, facilitates replenishment of the dissolved oxygen, since the gas already dissolved passes gradually into chemical combination with the rubber. The normal slowness of the diffusion process for passage of oxygen or air into rubber (whether natural or synthetic) is thereby circumvented. For reasons similar to the preceding, where rubber is to be submitted to further processing, *e.g.*, remilling or extrusion, storage in thin sheet, rather than in slabs or in compact rolls, is obviously advantageous.

THERMAL PLASTICIZATION

It has already been remarked that, in the absence of oxygen, relatively little plasticization is effected in natural rubber by moderate heating. The position with Buna-S or GR-S rubber is still more marked because of its tendency to undergo cyclization or cross-linking, with results roughly equivalent to those of prevulcanization or "scorching". This effect is possibly not quite absent from the behavior of natural rubber; Van Rossem[13], before 1917, showed that when plantation crepe rubber is heated at 130° C for 2–12 hours in a current of carbon dioxide, its solubility in benzene is markedly decreased, over 20 per cent becoming insoluble. There is a possibility, however, that this alteration may be associated at least in part with the drying effect of the treatment[14].

With Buna-S and GR-S rubbers the effect is certainly the outcome of cyclization or cross-linking, and, in contrast to the behavior of natural rubber, constitutes a serious counter-effect in the plasticization of Buna-S or GR-S by the aid of heat.

AUXILIARY FACTORS INFLUENCING THE OXYGEN-PLASTICIZATION OF RUBBER

Oxygen plasticization can be accelerated by raising the temperature of the rubber mass, but this advantage is largely discounted if the dissolved oxygen, as it becomes consumed, is not easily replaced. This consideration is particularly important for Buna-S and GR-S, which appear to call for larger proportions of oxygen for plasticization and yet dissolve oxygen less readily than does natural rubber. Hagen's comprehensive paper[15] in the relatively early days of Buna-S rubber stressed the importance of exposing the rubber in comminuted form, or better in the form of porous strip, to the atmosphere during thermal plasticization. The form of Buna-S recently described as Buna-S III has the porous or sponge strip structure, being obtained in this form by appropriate coagulation procedure during manufacture, and lends itself well to preplasticization by thermal treatment before milling.

The replasticization of vulcanized Buna-S and GR-S by thermal treatment in an analogous manner can be facilitated[16] by heating the material in crumb form so as to ensure effective contact with air, and then rapidly cooling and consolidating to arrest the oxidation process at the desired stage.

It is well known that factors other than temperature can modify the rate or degree of plasticization. Milling indeed is a factor perhaps as old as, and certainly more widely applied than, simple thermal treatment.

The effect of milling is more marked than would be expected from the temperature attained or from the more effective distribution of atmospheric oxygen throughout the mass. This is a particular advantage with the Buna-S and GR-S because it offers the possibility of increasing the oxidation effect without comparably increasing the cyclization process.

The reason for this effect of milling, which is also revealed by comparison of the curves in Figure 1, if allowance is made for the much lower temperature of the milling operation, is not at first obvious. From its aging behavior, however, rubber is well known to become more reactive when subjected to mechanical strain. Similarly it has been shown that breakdown by flexing is related to oxidative degradation[17].

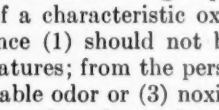
Evidence of the activation of rubber molecules or of segments of rubber molecules when the material is subjected to strain by milling can also be observed in the action of chemical agents such as sulfuric acid or sulfonic acids on rubber or gutta-percha, or even on replasticized vulcanized rubber; the chemical change proceeds much more rapidly when the mixture is continuously stressed than when the uniform mixture is heated at the same temperature under static conditions[18]. The applied strain appears to cause the development of increased chemical activity at some of the double bonds in the long chain molecules.

This chemical activation of the rubber towards atmospheric oxygen in milling probably accounts also for the possibility of plasticizing and sheeting vulcanized scrap of tube or tread quality, whether from natural rubber or GR-S stock. The treatment was extensively applied, under the name Penther process, in Germany during 1914–1918, for the reclaiming or regeneration of vulcanized waste[19]. The reclaim obtained by this milling process, on revulcanization, gives products much superior in physical and mechanical qualities to those from thermal reclaim from equivalent stock.

CHEMICAL ACCELERATING AGENTS

It is a striking fact that the substances which serve as socalled peptizing agents for rubber and which exert a plasticizing effect which cannot be explained by a mere physical or static influence such as swelling of, or dissolving in, the rubber or by a modification of the condition of the medium, *e.g.*, its pH, are themselves easily capable of oxidation. Nitroso compounds, substituted hydrazines and thiols are well known groups of such substances. Other features than the presence of a characteristic oxidizable group are, however, also necessary. The substance (1) should not be so volatile as to vaporize excessively at mixing temperatures; from the personal point of view, it should possess (2) no very objectionable odor or (3) noxious effect.

Feature (3) has proved an obstacle to the adoption of phenylhydrazine itself and of many of its derivatives which possess its plasticizing action. From the frequency with which its conversion into simple stable derivatives, *e.g.*, solid phenylthiobiazoline hydrosulfide:



by successive action of CS_2 and CH_2O, is accompanied by some loss of plasticizing action, it would appear that the latter is frequently dependent on the easy regeneration of phenylhydrazine during the milling process.

Some of the nitroso compounds of which *e.g.*, *p*-nitrosodimethylaniline is possibly the best known, are powerful plasticizers, but have an undesirable tendency to cause dermatitis and also interfere with the vulcanization process. The thiols, even when selected to show sparing volatility, are not wholly free from skin effect, and their odor is generally objectionable.

The commonest thiol in the rubber industry, *viz.*, mercaptobenzothiazole, like the commonest nitroso compound, entered it as an accelerator. Relative to most other thiols, mercaptobenzothiazole is almost inodorous. Its plasticizing activity, whether aided by static heating or by milling, was realized 15 years ago[20].

From the fact that these chemical softening agents are easily oxidizable, their action probably arises from an oxidation of the rubber "induced" by their own oxidation process. For this to occur the two reactions, in the plasticizer and in the rubber, respectively, must proceed at reasonably comparable rates. If the one primary oxidation were inordinately faster, its effect might be slight. This probably explains why some well known spontaneously oxidizable substances are not efficient plasticization catalysts.

These considerations postulate a gradual disappearance of the chemical plasticizer during the milling process. In the case of mercaptobenzothiazole, the product of the oxidation process is dibenzothiazyl disulfide, which still has valuable acceleration properties for vulcanization, although not identical with those of the parent substance. Chemical analysis indeed indicates that, after 15 minutes' cold milling of rubber containing 0.5 per cent of mercaptobenzothiazole, 97 per cent remains unoxidized, but that after milling for a further 20 minutes at 70° C, nearly half is oxidized, only 56 per cent of the mercaptobenzothiazole remaining as such. These figures hold, of course, only for the particular conditions obtaining in this experiment.

COMPLICATIONS WITH BUNA-S TYPES

With synthetic rubbers of the now common butadiene-styrene copolymer type, plasticization provides a more complex problem because of their tendency to undergo a change conveniently described as cyclization or cross-linking, without expressing any precise view as to the alteration in the molecular configuration. The effect on the solubility and plastic flow is similar to that of vulcanization.

This tendency of GR-S or Buna-S makes thermal treatment likely to give effects comparable with prevulcanization. Like unworked natural rubber, GR-S dissolves only fractionally in a rubber solvent such as benzene or petroleum naphtha, the soluble and insoluble fractions being denoted respectively as sol and gel. With cyclization the percentage of gel component in GR-S increases in magnitude. This may interfere with the behavior of any particular lot of GR-S towards, and in, rubber solvents. It may also have a detrimental influence on the ease of homogeneous blending of two stocks by dry milling; it can therefore be a source of irregular behavior of "compounds" made with the use of master batches or mother stocks. Recent results of Vila[21] suggest that a higher proportion of gel exerts a deleterious influence on the physical properties in the eventual vulcanizate.

In the plasticizing of GR-S rubber, therefore, by any process, and also in the reclaiming of vulcanized GR-S it is helpful to choose conditions as favorable as possible to the prevention of cyclization, *e.g.*, as low a temperature and as short a time of heating as is practical. Doubtless recent experience

has repeatedly impressed this. The underlying principles, however, were recognized with Buna-S and well stressed as early as 1938[15]. For the plasticization of Buna-S it was then shown that, as with natural rubber, oxidative softening was advantageous. Figure 3 shows the increased rate of plasticization of Buna-S (and also of its cyclization) with rise of temperature; Hagen suggests that the softening period should desirably be about 30 minutes so as

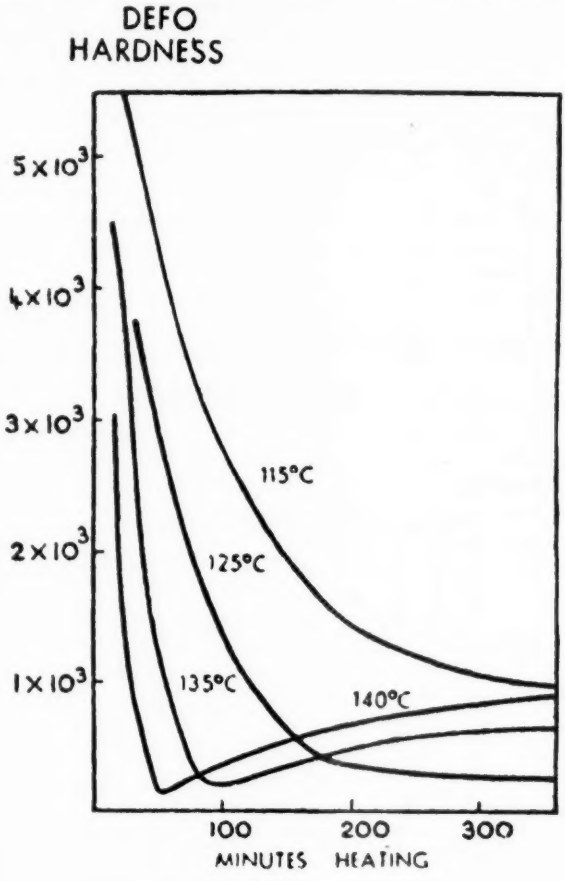


FIG. 3

to allow time for reasonable uniformity of effect and to prevent prolongation of cyclization. Adopting this period of 30 minutes, Figure 4 shows that no serious additional softening effect is gained above 150° C.

Figure 5 reproduces Hagen's results on the beneficial influence of increasing the air pressure to 3 atmospheres (preferably with concurrent mastication which helps to delay the onset of hardening with prolonged heating). Hagen's paper also demonstrates the advantages of using the rubber in the form of crumb or of porous strip (now represented by Buna-S III). Unspecified catalysts, applied superficially or incorporated by milling, increase the rate of the thermal oxidation and softening, but are utilized to lower the necessary temperature rather than to reduce the time below a limit of 30 minutes.

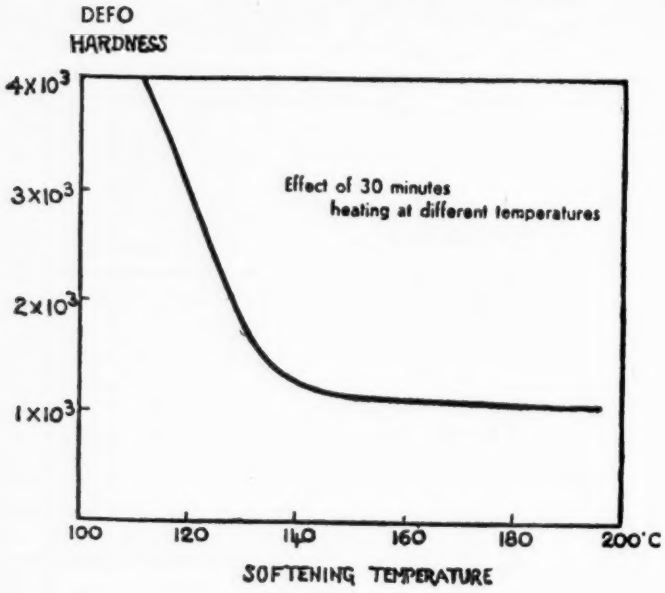

DEFO
HARDNESS
4X10³
3X10³
2X10³
1X10³
Effect of 30 minutes
heating at different temperatures
100
120
140
160
180
200°C
SOFTENING TEMPERATURE

FIG. 4

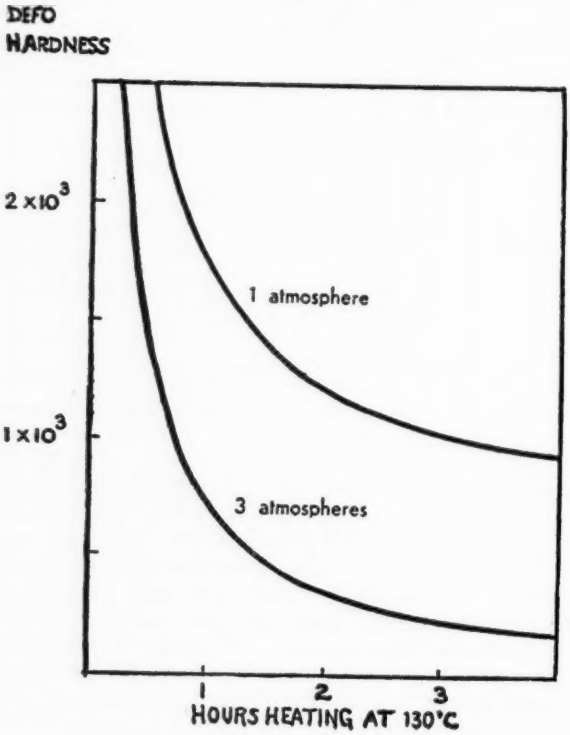

DEFO
HARDNESS
2X10³
1X10³
1 atmosphere
3 atmospheres
1
2
3
HOURS HEATING AT 130°C

FIG. 5

Hagen's paper nevertheless makes no mention of the fact that small proportions of oxygen may actually favor formation of the cyclized gel component in heated Buna-S, probably by some form of oxygen bridging of the molecules. To prevent this becoming the main effect it is necessary to have an ample surplus of oxygen so that the oxygen bridging is more than compensated by oxidative softening.

It is natural to wonder whether chemical agents cannot be found to prevent the undesirable cyclizing process which persistently runs counter to the desired plasticization effect. Negative catalysts for this purpose may be possible, but none seems to be known with certainty. Furthermore, if it is assumed that cyclization or cross-linking occurs through active bonds or segments in the "rubber" molecules, it appears likely that such activation may not be permanently associated with a particular structural fragment of a molecule, but may represent merely a portion with transiently acquired surplus energy, related to the intramolecular vibrations of the rubber molecule itself. The extensively branched Buna-S molecule is not as safe for such arguments, however, as the more linear natural-rubber molecule, and the possible existence of definite ethylenic bonds, groups or segments with a higher level of activity to serve as nuclei for cross-linkages or bridges cannot be disregarded, nor can the cognate possibility of suppression of the cyclization tendency by extraneous reactive chemical substances capable of preferentially attacking the active nuclei.

Statements from the Continent indeed indicate that chemical agents (under names which conceal their identity) have been used there during German occupation to prevent the hardening of Buna-S in storage, but whether these substances were negative catalysts, or "chemical stoppers", to the cross-linkage or cyclization process, or merely powerful plasticizing agents which contributed a softening effect even at ordinary temperatures[17], thereby compensating for the inherent tendency to hardening by cross-linkage, it is at present impossible to say.

ACKNOWLEDGMENT

The writer acknowledges permission from the Dunlop Rubber Co., Ltd., to publish this paper.

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OBJECTIVE LABORATORY TESTING OF THE PROCESSABILITY OF ELASTOMERS *

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The advent of synthetic elastomers, with their extreme variation in properties due to differences both in polymerization methods and in chemical composition, has resulted in considerable attention by the rubber technologist to the processing characteristics of each new type and modification. Not infrequently, new elastomers, although commercially advantageous in other respects, have been rejected by the fabrication plants because of poor processability. Development of improved elastomers has also been hampered by the time-consuming and costly factory-scale evaluations required to determine processing quality.

The growing importance of this particular aspect of polymer evaluation prompted an analysis of processing difficulties which are encountered in mixing, calendering, extrusion, and related operations. This analysis led to the development of a set of objective laboratory tests which, it is believed, will predict fairly accurately the factory-scale processing behavior of dry uncured compounds of elastomers. Of the diverse processing difficulties in the fabricating plants, building tack is believed to be the only important factor not covered by this investigation.

A number of useful processing tests, centered around subjective appearance ratings of tubed or milled specimens, speeds of extrusion, or plasticities, have been described in previous publications[1]. Although these tests are frequently useful for predicting specific types of behavior, there are several objections to their general use. First, they measure only a limited number of the important types of processing behavior and, second, the more comprehensive tests are subjective—that is, they depend to a large degree on the operator's opinion.

FACTORS INVOLVED IN PROCESSING

Types of processing behavior from which difficulties arise on the elastomer fabrication line are as follows:

1. *Mixing Operations.*—High power consumption during mixing, long mixing time, extended remilling time.

2. *Extrusion and Building Operations.*—Surface roughness, gauge increase, gross shape changes, tearing, excessive working temperature, lamination failure, hand-working difficulties, slow speed of extrusion.

A satisfactory set of laboratory tests must give information concerning all these types of behavior.

Analysis of these processing difficulties indicates that the following characteristics of the elastomer and its unvulcanized compounds are important.

1. Initial viscosity and the rate of decrease of viscosity during mixing operations. (By viscosity is meant the usual average viscosity, determined

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 37, No. 8, pages 767–769, August 1945.

on a large sample with conventional instruments such as the Mooney viscometer. This definition is necessary, since elastomer compounds possibly contain local variations in viscosity which may be important in judging processing behavior but which cannot be detected by available viscometers.)

2. Ease of incorporation of the filler (believed to be closely related to ease of wetting and dispersion[2]) by the polymer.

3. Viscosity of the final compound.

4. Tendency of the compound to retract after strain.

5. Local irregularity of flow and of distribution of strain in the compound during deformation.

The first three factors are involved primarily in the mixing operation. Higher rates of breakdown, greater ease of incorporation of the filler, and lower viscosity of the finished compound contribute to the attainment of lower power consumption, shorter mixing, and shorter remilling cycles.

The remaining factors, along with compound viscosity, are mainly connected with fabrication operations. Reduced retraction after fabrication stresses are released is conducive to less departure from the desired shape and dimensions, to reduced tearing, and to fewer lamination failures. Better uniformity of flow and of distribution of strain results in smoother surfaces, in reduced tearing (elimination of thin areas), and in better contact between laminates. Lower compound viscosity reduces work of forming, leads to reduced temperatures in extrusion and calendering, and permits more rapid fusion of laminations. Compound viscosity also is a factor which determines retraction and uniformity of flow and strain distribution, but is seldom the major factor.

An extended survey of factory-scale processing evaluations of experimental lots of GR-S has made it obvious that no single laboratory test can be expected to give information about all the above properties. For example, certain properties are often, but not always, antithetical, *i.e.*, when one property undergoes a desirable change the other undergoes an undesirable change. An example is found in factory processing operations on experimental GR-S samples A-1, A-2, and A-3[3].

Polymer	Mixing rating	Tubing rating
A-1	1 (best)	3
A-2	1	2
A-3	2	1 (best)

With a typical tire tread formulation the ratings of the three polymers were observed with respect to compatibility with black in factory mixing, and to the relative dimensions and surface appearance of the final stocks after tubing as tire treads. Here the polymer which was mixed with the greatest facility was extruded with the greatest difficulty, and *vice versa*.

Garvey and coworkers[4] also found that a GR-S compound may be very difficult to mix but can still be extruded satisfactorily. It should be emphasized, however, that such behavior is not universal, but occurs frequently enough, so two or more different types of laboratory tests are needed to obtain a full picture of processing characteristics.

For convenience, processing difficulties are here divided into two groups: those peculiar to compounding (mixing) and those involved in fabrication (calendering, extrusion, and lamination). Such a division is consistent with both factory production and the frequently contrasting behavior of a polymer in compounding and in fabrication.

TABLE I

CORRELATION OF LABORATORY WITH FACTORY RESULTS

	Laboratory results[a]				Factory results[b]	
	Filler stiffening[c] ($V' - V$)	Compound viscosity[c] (V'')	Length shrinkage (%)	Rugosity (mm. × 10^2)	Compounding	Fabrication
Group I (GR-S type)						
B-1	50(1)	67(1)	41(2)	130(3)	1(5)	3(5)
B-2	56(1)	64(1)	40(2)	55(2)	1	2
B-3	49(1)	66(1)	34(1)	23(1)	1	1
Group II (GR-S type)						
C-1	56(2)	61(2)	39(2)	42	2(6)	2(6)
C-2	43(1)	48(1)	36(1)	18	1	1
Group III (GR-S type)[d]						
A-1	29(1)	58(1)	50(2)	—	1(3)	3(3)
A-2	33(1)	55(1)	52(2)	—	1	2
A-3	44(2)	61(2)	45(1)	—	2	1
Group IV (GR-S type)[d]						
D-1	43(1)	48(1)	48(2)	—	—	2(7)
D-2	37(1)	54(2)	40(1)	—	—	1
Group V (GR-S type)						
E-1	30(1)	54(2)	40(1)	30(1)	1(8)	1(8)
E-2	34(1)	54(2)	42(1)	41(2)	1	3
E-3	28(1)	47(1)	43(2)	31(1)	1	2
E-4	32(1)	50(1)	45(3)	57(3)	1	4
Group VI (Perbunan type)[e]						
F-1	36(1)	74(1)	33(1)	49(1)	—	1(9)
F-2	44(1)	78(1)	38(2)	95(2)	—	2
Group VII (Perbunan type)[e]						
G-1	39(1)	83(1)	38(2)	140(2)	—	2(9)
G-2	37(1)	82(1)	34(1)	75(1)	—	1

[a] The measured value is given as the first number; the qualitative rating based on these values is given in parentheses.
[b] Numbers in parentheses are literature citations.
[c] Mooney viscosities measured at 212° F, with large rotor.
[d] These shrinkage measurements were made on stock calendered at 100° instead of 160° F.
[e] These stocks contained more softener and had longer milling than the stocks of GR-S type polymers.

SELECTION OF LABORATORY TESTS

Compounding Characteristics.—The principal aim in factory compounding operations is to obtain a finished compound at a specified viscosity in minimum time with minimum power consumption. Hence, some system of viscosity measurements appears logical as a laboratory test for mixing characteristics. A complete viscosity history of the mixing cycle would be ideal and would, it is believed, give considerable practical information about mixing behavior. The area under such a viscosity-time curve increases whenever the processing behavior during mixing is unfavorable. High initial polymer-viscosity raises the entire curve, low rate of breakdown raises all but the initial portion, and slow incorporation of the filler raises the maximum and subsequent portions. As the area under the curve increases, the power consumption must increase.

As a feasible compromise with the ideal, viscosities taken at several select points along the curve when using a fixed mixing cycle seem satisfactory. A successful testing procedure for studying experimental lots of GR-S and

Perbunan involves obtaining the viscosity of the polymer (V), adding filler (50 parts by weight of EPC black per 100 of elastomer) over 10 minutes, postmilling 10 minutes, obtaining the viscosity of the filler master batch (V'), adding softeners and curatives during 5 minutes, and obtaining the compound viscosity (V''). Since elastomers differ markedly[10] in temperature coefficients of viscosity, these viscosities should, ideally, be measured over the entire working temperature range; or, for practical control of a specific mixing and fabrication cycle, viscosities V and V' should be measured at the average mixing temperature, and V'' should be measured at the specific forming temperatures (temperatures of extrusion, lamination, moulding, etc.). Compounding was carried out on a 6 × 12 inch cold-roll mill and viscosities were obtained on the Mooney disk plastometer[11]. Other methods of determining the viscosity could be used—for example, the Williams parallel-plate plastometer[12] or the Mooney rotating-cylinder rheometer[13].

Master-batch viscosity V' anticipates the order of magnitude of compound viscosity V'' and, furthermore, is more sensitive to the fundamental mixing properties—rate of breakdown and ease of incorporation of the filler—since no softener has been added at this point. Therefore, viscosity V' is considered the more important of the two in characterizing processing behavior during mixing.

Since most elastomers are made to a specified initial viscosity (45–55 Mooney viscosity for GR-S), it is usually desirable to make processing comparisons at an equivalent viscosity. Using this viscosity method of determining relative compound behavior, the difference $(V'-V)$ between the master batch viscosity V' and the initial viscosity V is computed, a measurement here called "filler stiffening". The measurement $(V'-V)$ corrects the slight differences that may exist between the initial viscosities, and measures the combined effects of rate of viscosity reduction and ease of incorporation of the filler, the two important fundamental factors influencing overall mixing characteristics. High numerical values for $(V'-V)$ are indicative of poor mixing properties and low values of desirable behavior. For replicate mixing of a single lot of GR-S, $(V'-V)$ showed a coefficient of variation (ratio of standard deviation to the mean) of 10 per cent. (The coefficients of variation in this paper are based on not less than fifteen replicated tests, mixing and testing being done on the same day with the same materials, equipment, and operators.)

A similar quantity $(V''-V)$, employing the final viscosity, correlates well with $(V'-V)$, but shows greatly reduced sensitivity, the coefficient of variation being 29 per cent.

Coefficient of breakdown[14], defined as the ratio of viscosity reduction in a fixed milling time to the original viscosity, gives information about molecular weight reduction, but not about ease of incorporation of filler. Furthermore, the reproducibility of the test is rather poor, as the coefficient of variation is 50 per cent.

Banding time[15], the time necessary for the raw elastomer to form a hole-free band with milling, has been used with fair success in some laboratories for estimating general processability. This test might be construed as giving some indication of both mixing (breakdown rate) and fabrication properties (retraction and uniformity of flow). The principal objection, however, is that this test depends on the operator's opinion for the end point. According to our results, this test also shows poor reproducibility; the coefficient of variation obtained by the same operator is 25 per cent, and by different operators, greater than 50 per cent.

Fabrication Characteristics.—As pointed out, three properties of the elastomer compound appear to be largely responsible for the behavior of the compound during factory-scale fabrication operations—namely, the ability of the system to maintain the imposed gross shape after stress is released, to flow uniformly so as to eliminate surface roughness, and to flow under a minimum of stress at commercial rates of shear. To circumscribe these properties, measurements must be made of gross retraction (shrinkage) after stress is released, of roughness of the surface of the retracted sample, and of the viscosity of the sample. Of necessity commercial equipment operates at high rates of shear—that is, at stresses far above the yield point of the material. Therefore, viscosities at commercial rates of shear are of more value than yield points in this discussion.

TABLE II

CORRELATIONS FOR COMPOUNDING VARIATIONS

	Laboratory results[a]				Factory results[b]	
	$V'-V$	V''	% L.S.	Rugosity	Compounding	Fabrication
Group I						
Black No. 1	6(1)	55(1)	41(2)	22(2)	—	2(16)
Black No. 2	9(1)	52(1)	30(1)	8(1)	—	1
Black No. 3	6(1)	50(1)	46(3)	49(3)	—	3
Group II						
Black No. 1	6(1)	51(1)	41(1)	22(1)	1(*10*)	1(17)
Black No. 5	18(2)	69(2)	42(1)	35(2)	2	2
Group III (black content)						
20 parts No. 5	13(1)	48(1)	44(4)	68(3)	1	4[c]
40 parts No. 5	22(2)	49(1)	41(3)	29(2)	2	3
60 parts No. 5	36(3)	59(2)	29(2)	10(1)	3	2
80 parts No. 5	73(4)	72(3)	12(1)	6(1)	4	1

[a] The measured value is given as the first number and the qualitative rating as the second figure (in parentheses).
[b] Numbers in parentheses are literature citations.
[c] General factory-scale experience.

A satisfactory simple set of objective tests which successfully depicts large-scale fabrication behavior of an elastomer compound consists of obtaining compound viscosity V'', of determining the extent of with-grain retraction (length shrinkage) of a thin calendered sheet, and of objectively measuring the rugosity (roughness) of the surface of the retracted calender sheet.

Simple and reproducible means of making the sample for the length shrinkage and rugosity measurements involves banding the compound at 0.030–0.040-inch roll gauge on the middle roll of a two-roll, even-roll speed calender (additional rolls dropped from contact with the sample) while maintaining the roll temperature within 2–3° F of some fixed value (160° F). The stock is marked at convenient lengths (25 cm.) on the back of the middle roll near the nip by a notched wheel running on the stock. On either side of the marking wheel at 5-cm. distances are placed rotary knives, which cut the marked sheet to 10-cm. widths. After constant temperature is attained in the working stock, six marked sections are cut from the marked band either as individual sections or as groups of two or three. These sections are allowed to shrink freely at room temperature, top-roll face up, on a talced, smooth, level surface for 16 hours (shrinkage is actually 90 per cent complete at the end of 15 minutes for GR-S compounds, but the longer time is used because it gives complete shrinkage). As a refinement of this method the specimens are free-shrunk in

a constant-temperature water bath maintained at the calendering temperature. Except for high-melting crystallizable substances, such as balata, this refinement has not been deemed necessary.

The sample prepared in this manner is examined for length shrinkage (with-grain retraction) and rugosity. The length shrinkage is calculated as the percentage decrease in length:

$$100\ (L_o - L_s)/L_o$$

where L_o = unshrunk length (25 cm. for the example given)
L_s = average length between notched wheel marks on fully shrunk sample (cm.)

The rugosity (roughness) of the top-roll face of the same specimens is determined by the Mooney rugosimeter[18], an instrument which gives, on the basis of some assumptions of regularity of the surface roughness, the average hill height in millimeters.

The coefficients of variation for the three tests on a mix-to-mix replication were found to be 2 per cent for length shrinkage, 14 per cent for rugosity, and 4 per cent for compound viscosity. To obtain such good reproducibility, control over the mixing operations must be exercised, such as fixed times for addition of ingredients and reasonably constant-temperature rolls. As with filler stiffening ($V' - V$), high numerical values for length shrinkage, rugosity, and compound viscosity point to poor processing characteristics.

Another method of obtaining a complete picture of fabrication characteristics would be the Garvey tubing index test[14], along with measurement of percentage swell of the tubed piece after retraction to equilibrium[14], and measurement of either the viscosity or the extrusion speed of the compound. However, from the viewpoint of routine testing, the extrusion method of making the test-specimen has two inherent difficulties: first, any estimates of roughness and irregularities of surface, important characteristics with respect to fabrication, are subjective; second, a small laboratory extrusion machine is not easily operated at a constant extrusion rate and a constant temperature.

Another possible method for obtaining gross retraction after strain is the Williams recovery test.[12] In a few exploratory comparisons it has shown good correlation with both laboratory and factory-scale observations of length shrinkage. However, the test has not been shown to give information concerning rugosity, a property which probably commands more universal attention in the practical field than length shrinkage.

CORRELATION OF LABORATORY AND FACTORY DATA

Four objective laboratory tests on a new polymer—filler stiffening, compound viscosity, length shrinkage, and rugosity—have been postulated as giving a fairly complete picture of the way in which a polymer behaves relative to a well-established control polymer in factory processing.

To determine whether the set of tests gives a qualitatively correct answer, advantage was taken of extensive factory processing information accumulated on many of the new synthetic elastomers produced during the past two years. In every case cited in Table I, the laboratory tests were made on samples of the identical polymers used in the factory evaluations. According to common procedure, factory ratings are relative only (1 is best, 2 is next, etc.) and are limited to intragroup comparisons. However, comparisons between groups can be made by use of measured values from laboratory tests. If proper

standardization of sample preparation and instrument calibration has been made, comparison of results from different laboratories is also possible.

Inspection of the correlations in Table I shows that it is impossible to predict in every case the observed factory behavior by any one of the laboratory tests, since a combination is necessary for the most complete evaluation. For example, neither compound viscosity V'' nor filler stiffening predicts differences between B-1, B-2, and B-3, or between E-1, E-2, E-3, and E-4. Likewise length shrinkage (percentage L.S.) will not detect the large processing difference between B-1 and B-2. Rugosity, on the other hand, does not differentiate between E-1 and E-3.

Major compounding changes on which factory processing data are available also have been checked by these laboratory tests for correlation purposes. As Table II shows, the laboratory tests predict factory behavior in every case.

SUMMARY

An analysis is made of the types of adverse behavior encountered in compounding and fabricating dry-mixed elastomers on a factory scale, with an attempt to ascribe the different modes of behavior to semifundamental properties of the elastomer and its compounds. On the basis of this analysis, four simple tests—filler stiffening, compound viscosity, length shrinkage, and rugosity—are proposed for determining the processing properties of elastomers on a laboratory scale. Extended correlations of predictions made from these tests with factory data demonstrate their reliability and usefulness in laboratory evaluation of new rubberlike materials.

Much of the background information referred to in this and the following paper (page 833) was accumulated by the rubber industry at large working on the government-sponsored rubber program through the Research and Development Section, Rubber Reserve Company, and therefore has been subject to the usual secrecy orders. For this reason much of the earlier literature has not been published in the usual channels. However, every effort has been made to recognize contributions, made but not released, by other investigators by reference to their names and organizations.

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GEL AS A DEFINITIVE PROPERTY IN GR-S TECHNOLOGY*

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Along with the many other fundamental properties of GR-S type polymers —molecular weight, molecular weight distribution, branching, space isomerism, and other structural irregularities—the significance of the presence of a benzene-insoluble species with an extremely high molecular weight on the general utility of the elastomer has been the concern of many investigators in the field[1]. This insoluble fraction, commonly termed "gel", swells in benzene or similar solvents and tends to break down under shear, either to soluble molecules or to dispersible units, as is shown plainly by enhanced solubility and increased swelling volume. The structure of gel in GR-S has not been demonstrated conclusively. Although most investigators favor a three-dimensional cross-linked structure, the gel may consist of substantially linear molecules with extremely high molecular weight.

Gel may be formed in GR-S during polymer-manufacturing operations or during plastication and mixing of the finished polymer. In the dry polymer the gelation or "network-forming" reactions become appreciable at temperatures[2] above 250° F. Presence of a small amount of oxygen catalyzes the gelation. On the other hand, oxygen also causes a simultaneous scission reaction, the rate of which is proportional to oxygen concentration; hence, large amounts of oxygen reduce the net rate of gelation.

The purpose of this paper is to report and discuss the results of an investigation to determine the significance of the gel portion in relation to several important practical properties of GR-S.

DETERMINATION AND CHARACTERIZATION OF GEL

Methods for the determination of gel content have been evolved over a period of two or three years. The background work for this paper was based on gel data from the method of Ewart and Tingey[3] which involves continuous extraction of a 0.20-gram sample by benzene of about 80° C. Later this was superseded by the Baker and Mullen method[4] and its modification, which is now more widely used in the industry. The latter method employs static extraction of a 0.20-gram sample in benzene at room temperature, possibly because of the higher extraction temperature[5]. In the former method, some differences between the results from the two methods have been noted on occasional samples[6]. However, data obtained in the present study indicate that the two methods may be used interchangeably for gel studies of this type.

The mechanical setup of the Baker and Mullen method permits measurement of the equilibrium "swelling index" of the gel—namely, the ratio of the weight of the swollen gel to the weight of the dry gel. The swelling index is related to the density of points of immobility (cross-links, entanglements)

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 37, No. 8, pages 770–775, August 1945.

between and within chains, high values of the swelling index being indicative of low density, *i.e.*, loose gel, and *vice versa*.

A second method of discriminating between loose and tight gels, now to be described, involves determining whether the gels become dispersible as the result of shear during normal factory fabrication. To simulate such shear in the laboratory, a treatment of ten cold mill refinings (a refining is one pass through rolls of clearance of 0.010 inch) was adopted. Gel which remains insoluble after this treatment is here termed *B gel;* that which disperses is called *A gel.*

Investigation of the connection between swelling index and A and B gel contents revealed (Figure 1) that B gel rarely occurs in GR-S in which the

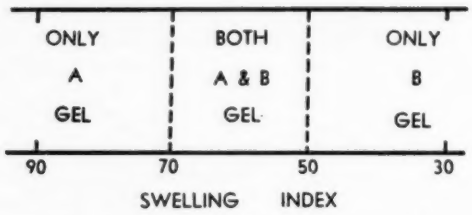

FIG. 1.—Relation of A and B gel with swelling index.

total gel (A + B) has a swelling index above 70. If the swelling index of the total gel is below 50, it is found to be largely B gel. The total gel in the intervening region contains both A and B gel. In all, approximately one hundred samples have been studied, and only one sample has been found which does not fit this classification. The abnormal sample was shown to contain B gel, even though the swelling index of the total gel was 85.

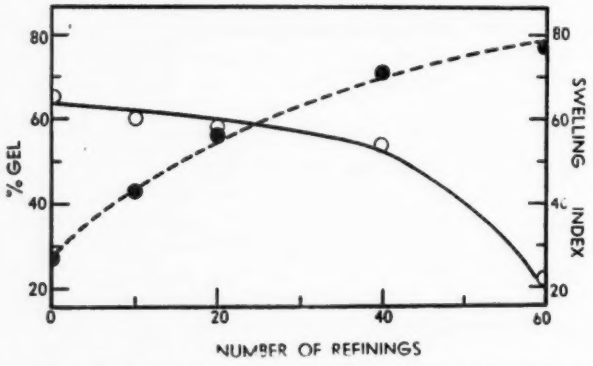

FIG. 2.—Effect of refining on gel content (—○—) and swelling index (- - -●- - -).

The behavior of a tight gel during continued shear is exemplified in Figure 2 in which a polymer, initially containing 60 per cent gel with swelling index of 25, is repeatedly cold-refined. The important features are that the swelling index increases with the number of refinings, an indication of the gradual disintegration of points of immobility between chains, and that gel content does not decrease appreciably until the swelling index has risen to 70.

It is to be emphasized that A and B gel are believed to differ only in degree, not in kind. In other words, B gel is thought to be A gel in which the density of the points of immobility has been greatly increased. In fact, the higher the A gel content of the polymer, the earlier the development of B gel occurs. For example, in a comparison of GR-S polymers 1 and 2, containing 34 per cent A gel (swelling index of 96) and no gel, respectively, polymer 1 showed a considerably advanced development of B gel during Banbury plasticization at 320° F, as Figure 3 shows.

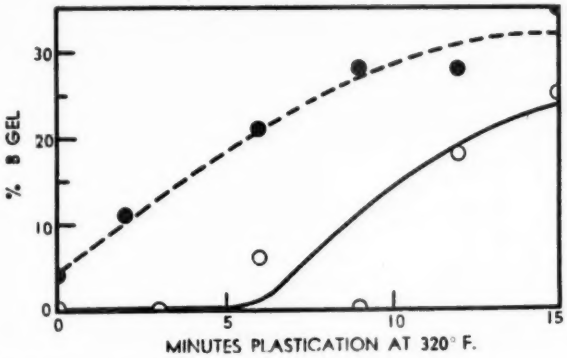

FIG. 3.—Development of B gel in high A gel (- - - ●- - -) and low A gel (—○—) polymers.

GEL AND TECHNICAL PROPERTIES

This investigation has been concerned primarily with the correlation of gel content with the important processing properties of GR-S (filler stiffening, length shrinkage, rugosity, and compound viscosity) and with the significant physical properties of its vulcanizates (tensile, elongation, modulus, and cut growth). Methods of measuring the specific processing properties and their implications in factory-scale production are discussed in another paper[7]. The conventional Scott testing equipment was used for determining the stress-strain properties of the vulcanizate. Cut-growth life was measured by determining the number of bending cycles required to propagate an initiated crack to a length of one inch, the bending cycle being 0° to 90° to 0°.

Early attempts to correlate technical properties with total gel content, without further characterization, did not yield conclusive evidence. Frequently samples of GR-S containing 40–50 per cent gel exhibited unusual properties, but other lots having similar gel contents possessed normal properties. This anomalous behavior prompted investigation of the possible existence of different kinds of gel, which led to the conclusion, cited above, that gels could differ in degree (density of cross-linking) but probably not in kind.

Effects of Loose (A) Gel.—From a reëxamination of our preliminary data, taking into consideration the degree of cross-linking, it was found that gels of swelling indices greater than 70 (A gel) exerted no detectable influence on properties. Presumably the A gel was destroyed (or dispersed) during the low-temperature laboratory mixing cycles. As Figure 3 shows if processing temperatures are high, high initial content of A gel leads to early appearance of B gel.

However, Gross, Tierney, and Vila[8] showed and Baker[9] confirmed, in a large sample study, that even loose gel (A gel) exerts small influence on process-

ing and physical properties, although it is probably dispersed during mixing. If the gel is reduced to normal molecular sizes, there may be a different distribution of chain lengths and changes in the branching which should lead to a different material, but these changes are of minor practical importance.

Effects of Tight (B) Gel.—Once the importance of density of cross-links in relation to persistency of gel during compounding was recognized, the correlation between tight gel and properties became more clear-cut. Preliminary data, obtained on several commercial lots of GR-S manufactured in such a manner as to contain tight gel, indicated that the presence of a substantial quantity of B gel in a tread compound improved; *i.e.*, it lowered the length shrinkage and rugosity, but adversely influenced other properties, such as increasing the filler stiffening, compound viscosity, and modulus, and lowering the elongation and cut-growth life. A typical comparison is that of GR-S 2 and 3 of Table I. Generally speaking, B gel improved calendering and extru-

TABLE I

EFFECT OF B GEL ON PROPERTIES OF GR-S

GR-S No.	2	3
B gel (percentage)	0	45
Swelling index of B gel	—	27
Processing properties		
Filler stiffening	40	65
Length shrinkage (percentage)	45	31
Rugosity (mm. × 10^2)	66	27
Compound viscosity	67	83
Vulcanizate properties		
Stress[a] at 300% (lbs. per sq. in.)	700	1300
Tensile strength[a] (lbs. per sq. in.)	2350	2050
Elongation[b] (percentage)	460	370
Cut-growth life, kilocycles		
At 2% combined S	330	110
At 600 lbs. per sq. in., 300% strain[b]	290	170

[a] At 2% combined sulfur (cured 240 minutes at 292° F).
[b] Values estimated for a fixed modulus by interpolation from a range of cures.

sion properties but placed properties of the vulcanizate at a disadvantage. Of course, the high modulus and low elongation could be corrected by proper compounding (reduction of combined sulfur, etc.), but the disadvantage in cut-growth life persisted, as shown by the comparison made at constant modulus.

Such comparisons are open to the objection, however, that the observed differences might not be due to gel but to other changes made in the polymer during polymerization. Probably a more reliable method of ascertaining the importance of gel is studying the properties of a single lot of GR-S as its gel content is increased progressively—for example, by heat plasticizing GR-S at about 320° F in a Banbury mixer.

Individual samples of GR-S 2 and GR-S 4, both gel-free and representing normal production of two plants, were heat-plasticized 0, 5, 10, 15, 20, 30, 45, and 60 minutes at 320° F (stock temperatures) in a laboratory Banbury mixer of 1000-cc. capacity. As controls, separate samples of each lot were plasticized on cold mill rolls (stock temperatures of 100–120° F) for 0, 20, 40, and 60 minutes, conditions under which experience has shown that no gel is formed. The use of cold-masticated polymers as controls was believed necessary to compensate for structural and molecular weight changes resulting from mastication. The pertinent data on the plasticized samples, after compounding in

TABLE II

CHANGE OF PROPERTIES OF GR-S[a] WITH TIGHT (B) GEL CONTENT

	Banbury plasticization at 320° F								Cold-roll plasticization (100–120° F)			
Plasticization time (min.)	0	5	10	15	20	30	45	60	0	20	40	60
Gel characteristics												
Total gel (percentage)	0	17	24	28	34	39	41	44	0	0	0	0
Swelling index	—	155	85	49	36	24	27	23	—	—	—	—
B gel (percentage)	0	0	0	22	30	38	40	46	—	—	—	—
Insol. with 50 black[b] (percentage)	24	28	32	37	42	47	47	51	—	—	—	—
Processing properties												
Uncompounded viscosity[c]	50	50	45	41	36	29	27	27	50	42	37	35
Filler stiffening	38	38	42	49	55	63	68	70	44	43	42	43
Length shrinkage (percentage)	42	43	43	40	35	28	20	17	45	43	41	40
Rugosity (mm. × 10^2)	35	34	30	17	8	7	5	5	36	31	21	15
Compound viscosity[c]	70	65	64	67	64	66	66	64	65	63	61	60
Vulcanizate properties												
Stress at 200%[d] (lbs. per sq. in.)	900	850	900	950	1100	1200	1300	1350	800	900	1000	800
Tensile[d] (lbs. per sq. in.)	2700	2700	2550	2200	2200	2050	1950	1900	2400	2200	2200	2500
Elongation[d] (percentage)	400	390	340	350	310	290	270	250	380	320	330	370
Cut-growth life (kilocycles)												
At 2% combined S[e]	55	75	50	30	15	10	5	5	67	58	55	61
At 600 lbs. per sq. in., 200% strain	110[e]	100[e]	90[e]	60[e]	40[e]	30[e]	20[e]	15[e]	90	85	90	125

[a] Recipe, parts by weight: GR-S, 100; EPC black, 50; liquid coal-tar softener, 5; zinc oxide, 5; mercaptobenzothiazole, 1.5; sulfur, 2.
[b] Percentage of polymer insoluble in the 50 EPC black master batch.
[c] Mooney viscosities at 212° F, with large rotor.
[d] At 2% combined sulfur (cured 240 minutes at 292° F).
[e] Averages of two mill mixes on same samples instead of the usual single mixes on two different samples.
[f] Values estimated for a fixed modulus by interpolation from a range of cures.

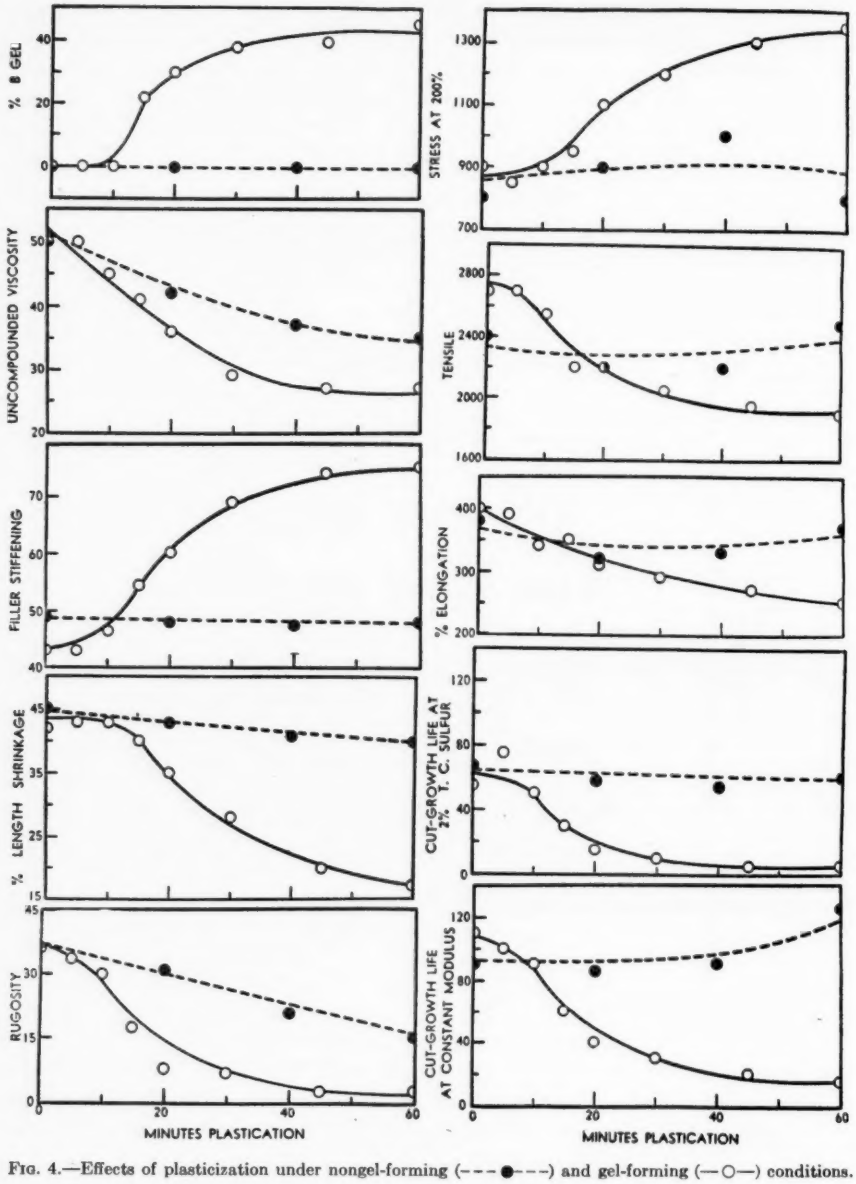

FIG. 4.—Effects of plasticization under nongel-forming (- - - ●- - -) and gel-forming (—○—) conditions.

a conventional tread test recipe, are given in Table II as the averages of the values obtained on the two samples for each plasticization time.

Most of the data are plotted in Figure 4, in which the solid line represents the changes for the samples plasticized under gel forming conditions (320° F) and the broken line for the samples plasticized under nongel-forming conditions (120° F). No effort has been made to indicate the reproducibility of the

value by the size of the circles. However, a test of the significance of the differences within a given series can be made with the following percentage coefficients of variation (ratio of standard deviation to mean): gel, 4; swelling index, 7; uncompounded viscosity, 4; filler stiffening, 10; percentage length shrinkage, 2; rugosity, 14; compound viscosity, 4; stress at 200%, 14; tensile strength, 10; percentage elongation, 5; cut-growth life, 24.

The replication errors between series are slightly larger as a consequence of day-to-day uncontrolled variations in mixing, curing, and testing conditions, as indicated by the initial (0 minutes plasticized) values of Figure 4 and of Figure 7.

These graphs show that increasing the B gel content of a polymer:

a. Increases filler stiffening
b. Decreases length shrinkage
c. Decreases rugosity
d. Increases modulus
e. Decreases tensile
f. Decreases cut-growth life

As shown in the discussion of Table I, the presence of large proportions of tight gel is particularly helpful for the processing operations of calendering and extrusion. The magnitude of the improvement in length shrinkage and roughness is shown in Figure 5; the samples portrayed are the calender test-specimens from one of the series of polymers used in this investigation. The original (unshrunk) length of these specimens (10 inches) is indicated by the bracketed arrows at the sides of Figure 5.

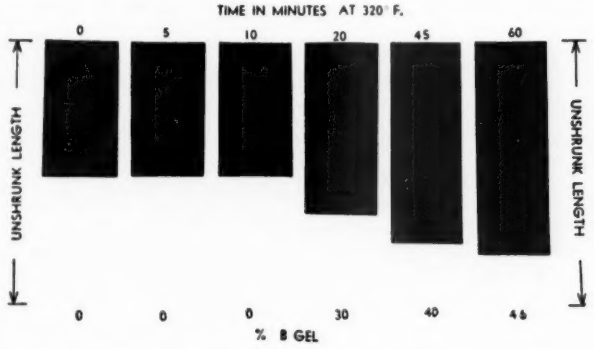

FIG. 5.—Changes in length shrinkage with plasticization at 320° F.

Not all of the length shrinkage and rugosity improvements can be ascribed directly to gel. From comparison with the control (120° F) curves, some of the improvement must be due to the lower Mooney viscosity of the uncompounded polymer. Furthermore the intrinsic viscosity (a function of an average molecular weight close to the weight average) of the soluble portion in gelled polymers is much lower than would be expected from Mooney viscosity measurements (Table III). The soluble mobile portions of these partially gelled GR-S samples have average molecular weights fully 50 per cent lower than would be anticipated from the Mooney viscosities of the total polymer. Of course, the effects are still due indirectly to gel, because gel formation removes mostly the soluble fractions of higher molecular weight. This latter point is amply supported by experiments on gelation of individual polymers in which the intrinsic viscosity of the soluble fraction is shown to drop rapidly as gel formation begins[10].

Some of the properties studied are so interrelated that one property varies simply because the other is influenced by gel. For example, since modulus is increased by gel, either tensile or elongation or both must reflect this change in modulus. These data point to a decrease in tensile strength rather than in elongation, although the correlation is not too clear-cut. Another case in point is that of rugosity and length shrinkage. Part of the drop in rugosity is due unquestionably to reduced length shrinkage. Further, cut-growth life is

TABLE III

MOONEY VISCOSITY AND SOLUTION VISCOSITY

Polymer No.	Percentage gel	Mooney viscosity	Intrinsic viscosity of soluble portion[a]
4	0	35	1.70
5	0	30	1.60
6	0	25	1.50
7	0	20	1.35
8	0	15	1.20
9	0	10	1.00
10	30	36	0.90
11	38	29	0.80
12	44	27	0.70

[a] Intrinsic viscosity $= c \xrightarrow{\text{limit}} 0 \frac{t - t_0}{t_0 c}$

where t = time of efflux for polymer solutions in benzene
t_0 = time of efflux for benzene
c = concentration of polymer, grams per 100 cc. solution

susceptible to modulus changes, increased modulus resulting in reduced cut-growth life. In this case, however, the interaction with modulus can be removed conveniently, as was done in the tabulation and plot of cut-growth life at constant stress of 600 pounds per square inch at 200 per cent strain.

THEORY OF EFFECTS OF GEL

The manner and degree in which the several properties are affected by increasing amounts of tight gel suggest the possible explanation that the filler, *e.g.*, carbon black, cannot be dispersed on the tight (B) gel portion and, therefore, is dispersed only in the soluble portion. This results in an increased carbon black loading on the soluble portion and should, as shown by experience on completely soluble polymers, increase filler stiffening and modulus and decrease length shrinkage and rugosity. The decreased tensile and cut-growth life may result from the poor tear resistance and general weakness of the black-free, tightly cross-linked, microscopic gelled areas (the properties of such areas should not be greatly different from those of a vulcanized gum stock of GR-S).

Support for the above exclusion theory was obtained through calculations kindly furnished by Baker[11]. He found that the average elemental volume in a gel of swelling index of 100 (well above the tight gel region) is probably less than the volume of the average EPC black particle which, therefore, cannot enter it without rupture.

Experimental support for the theory was obtained from a study of the influence of EPC black loading on length shrinkage and rugosity (Figure 6) for a 100 per cent soluble polymer (No. 13) and a 45 per cent B gel polymer (No. 14) of approximately equal Mooney viscosities. For the latter there are earlier reductions in both properties as the black loading is increased. This

behavior suggests an apparent increased filler loading which may be a combination of the contribution of gel as a filler and increased black loading in the soluble polymer. Also, if one considers the relative values at low loadings (less than 50 parts by weight) for which the curves approximate linearity, a loading of black in polymer 14, approximately one-half of that in polymer 13, results in even better properties. At extremely high loadings (60–100 of

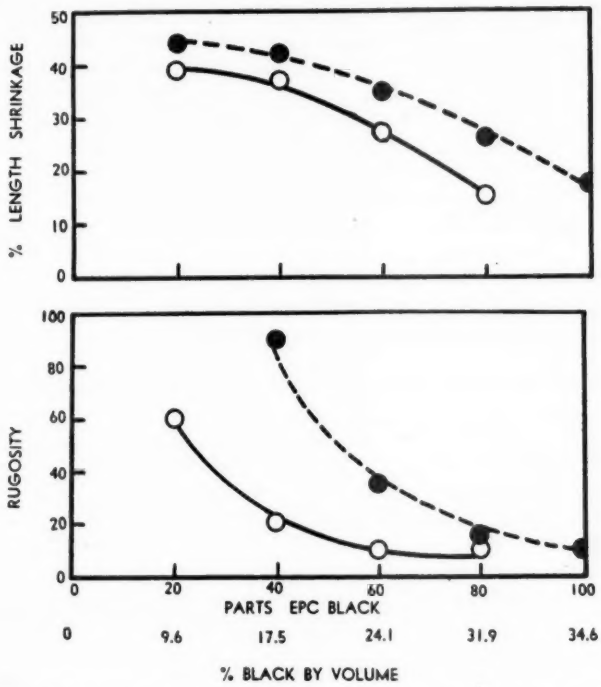

FIG. 6.—Variation of shrinkage and rugosity with black loading for gel (—○—) and nongel (- - -●- - -) polymers of the same viscosity.

black) this relation does not hold. Here, however, as a result of longer milling times and higher shearing stresses, the gel is probably being more and more disintegrated and its effect necessarily reduced. Evidence that the gel acts as a filler may also be obtained from extrapolation of the curves to zero loading, where the gelled polymer undoubtedly is superior.

Another method for checking the validity of the exclusion theory is to determine the effects of gel when it is formed only after the added filler has been normally dispersed. Gel so formed would not be expected to give a final compound with areas in which filler was concentrated and other areas in which filler was absent. On the basis of the theory the effects ascribable to gel present in the stock before compounding would not be noted.

Attempts to build up substantial quantities of gel with 50 parts of EPC black present were only partially successful. As Table IV and Figure 7 show, the decrease in solubility during plasticization at 320° F for black master batches (solid line) is much less than for the pure-gum polymer of Table II (broken line). The 5–10 per cent decrease in solubility is not sufficient to lend con-

TABLE IV

BANBURY PLASTICIZATION AT 320° F, UNDER GEL-FORMING CONDITIONS, IN THE PRESENCE OF BLACK

Plasticization time (min.)	0	5	10	15	20	30	45	60
Insoluble with 50 black[a] (percentage)	22	28	29	32	30	30	34	34
Processing properties								
Length shrinkage (percentage)	44	47	47	49	49	50	50	50
Rugosity (mm. × 10^2)	51	41	25	26	18	21	21	15
Compound viscosity[b]	70	62	56	55	52	51	48	44
Vulcanizate properties								
Stress at 200%[c] (lbs. per sq. in.)	700	750	750	750	750	650	650	650
Tensile[c] (lbs. per sq. in.)	2250	2250	2200	2150	2450	2250	1900	1850
Elongation[c] (percentage)	380	350	330	350	340	330	310	300
Cut-growth life (kilocycles)								
At 2% combined S	85	85	90	70	70	65	50	55
At 600 lbs. per sq. in., 200% strain[d]	115	95	80	75	75	70	50	45

[a] Percentage of polymer insoluble in 50 EPC black master batch.
[b] Mooney viscosities at 212° F, with large rotor.
[c] At 2% true combined sulfur (cured 240 minutes at 292° F).
[d] Values estimated for a fixed modulus by interpolation from a range of cures.

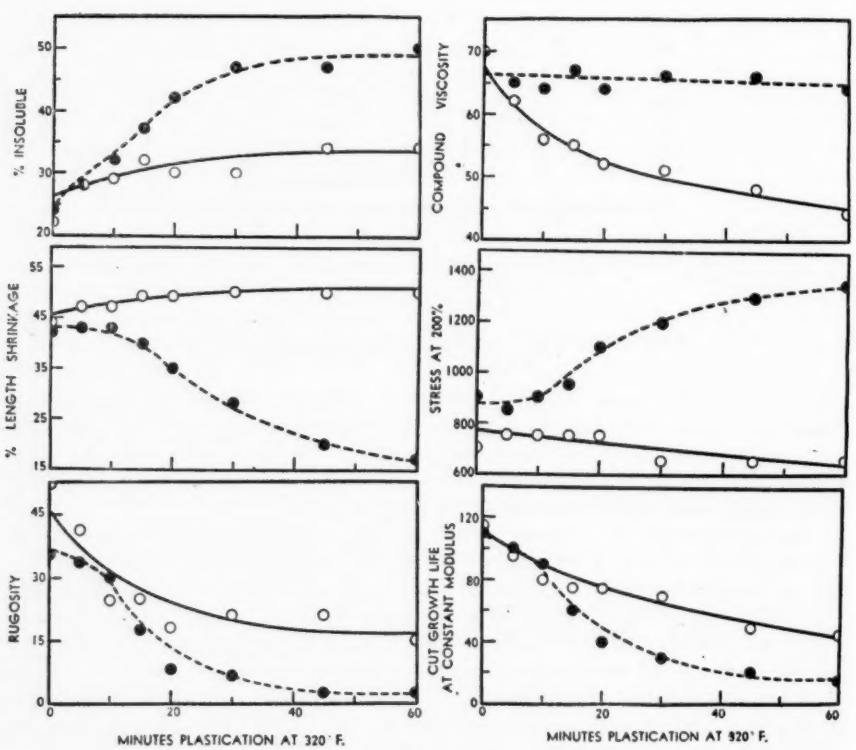

FIG. 7.—Comparative effects of plasticizing without (- - - ●- - -) and with (—○—) EPC black at 320° F.

clusive support to the proposed theory. With that reservation in mind, however, the behavior of most of the properties is in line with expectations based on the following theory. Length shrinkage increases rather than decreases, rugosity does not change more than might be expected from viscosity reduction, compound viscosity drops rapidly instead of remaining substantially constant, and modulus decreases rather than increases. The reductions in tensile, elongation, and cut-growth life are not easily explained on the basis of the theory, although they may have resulted from larger reduction in molecular weight than was obtained for equal times of plasticization under nongel-forming conditions (compare compound viscosities of this series with the series of Table II, plasticized at 120° F).

A propos of the 20–25 per cent insoluble polymer in the carbon black master batches plasticized 0 minutes, it should be pointed out that with GR-S, as with Hevea[12], channel black partially insolubilizes the polymer in the form of socalled bound rubber. The figure of 20–25 per cent bound rubber, using 50 parts of EPC black in a 100 per cent soluble GR-S, is in agreement with the observations of Baker and Walker[13] and of Lawrence and Hobson[14].

As to why the presence of the EPC black during plasticization should reduce gel formation, it is believed that at least two factors may be operative. First, channel black, because of its great adsorptive capacity and the presence of surface impurities, may retard gelation by adsorption and inactivation of the intermediates and thus cause gelation. Second, the relatively higher and more localized shearing stresses during mastication of the black master batch, contrasted to those during mastication of the raw polymer, may under the conditions in question destroy or disperse the gel nearly as fast as it is formed.

The practical implications of this comparison of plasticizing of GR-S at 320° F in the absence and in the presence of black should not be overlooked. For short heat-treatment periods (up to 15–20 minutes at 320° F), which are common to many factory processes, the advantages and disadvantages of having black present are almost insignificant. For extended heat treatment periods (30–60 minutes at 320° F), however, the presence of the filler is particularly an advantage for protection of final properties of the vulcanizate (modulus and cut-growth life). On the other hand, the presence of black is a disadvantage in that the processing improvements are not nearly so great (particularly as to length shrinkage and rugosity).

SUMMARY AND CONCLUSIONS

1. Of the gel fraction that may occur in GR-S, only that portion which has low swelling volume in benzene—tight (B) gel—markedly affects processing behavior and quality of product.

2. As the proportion of tight (B) gel increases, mixing operations become more difficult, and the quality of the final vulcanizate is lowered; specifically, decreased tensile strength, increased modulus, and decreased cut-growth resistance result. Where maximum quality is desired, processing conditions which favor the formation of tight gel should be avoided.

3. Conversely, appreciable amounts of tight (B) gel aid the processing operations of calendering and extrusion by reducing shrinkage and roughness. Where ease of processing is paramount and quality defects can be tolerated, heat-plasticization cycles which favor gel formation may be used to advantage.

4. To account for the observed effects of tight gel, the theory is advanced that fillers cannot enter this gel portion. This explanation is supported by a limited amount of direct evidence.

5. Heat-plasticization studies of GR-S at 320° F in the presence and absence of carbon black indicate that the black reduces the tendency to gel formation. For short heat treatments, common to many factory processes, the effect has no significance. For extended heat plasticization, incorporation of the black first may be either advantageous or detrimental, depending on whether maximum quality or ease of processing is the end objective.

ACKNOWLEDGMENT

The authors wish to thank A. W. Meyer, W. R. Dunn, L. F. Swec, M. C. Brooks, and R. M. North, of these laboratories, for their many contributions toward designing and producing special types of GR-S on which the foundation of this work was built.

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RUBBER PHOTOGELLING AGENTS *

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Solvents for use in photogelling experiments have been classed as active and inactive[1], the former comprising halogenated hydrocarbons and mixtures containing polar solvents, the latter the hydrocarbons. It would seem from the experiments to be described that insufficient attention has been paid in earlier work to the choice of solvents[2]. In the majority of experiments on record, an active solvent has been used, or an activator (aldehyde, ketone, or quinone) has been added to reduce the time necessary for gelation, which, with inert solvents and without activator, may require many weeks' or months' insolation. For this reason the specific effect of some agents has been obscured by the presence of others or by the solvent, and has given rise to contradictory reports. This applies particularly to molecular oxygen and sulfur.

As a preliminary it was found necessary to extend the data available on the rate of gelling of rubber in inert solvents.

INSOLATION WITH INACTIVE SOLVENTS AND WITHOUT ACTIVATORS

Experiments have been made with a variety of hydrocarbon solvents, including benzene and homologues, cyclohexane, decalin, tetralin, and light petroleum (b.p. 60–80°). The air was removed as completely as possible before sealing the tube and before the rubber had dispersed by boiling off a little of the solvent under reduced pressure. Under these conditions gelation by insolation is always extremely slow, requiring 60–100 hours' exposure to direct sunlight in summer months. Firm gels are seldom obtained. Generally, no change is noted for the first 20–30 hours' exposure, after which the viscosity gradually increases to a ropy consistency or semigelled condition. The tendency to gel is influenced by the solvent. Gels form most readily in toluene, *o*-xylene, mesitylene, cyclohexane and light petroleum, less readily in *p*-xylene, and still less in *m*-xylene; they have never been obtained without activators in cyclohexene, tetralin, or decalin. Benzene, toluene, and cyclohexane are suitable, since they are generally good solvents, both for rubber and for various activators.

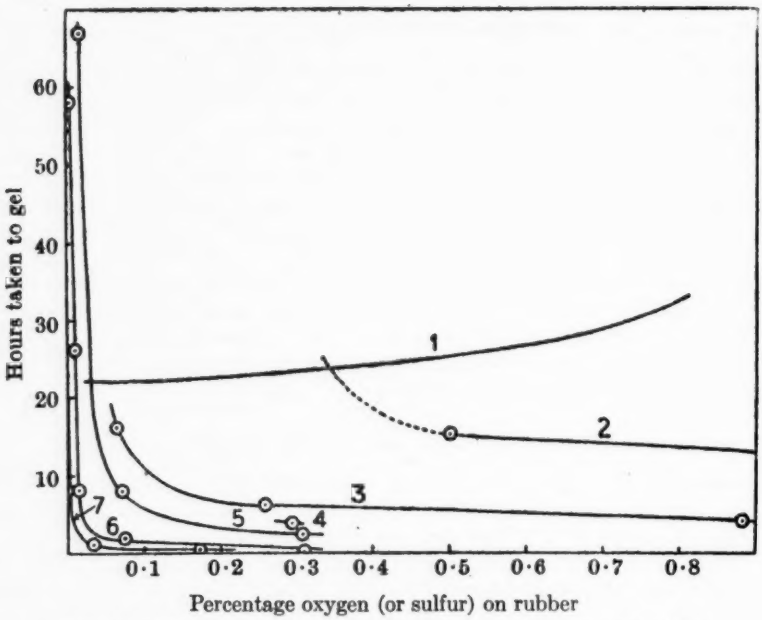
INSOLATION WITH KETONIC AND QUINONIC ACTIVATORS

A variety of these have been tried and need not be discussed in detail. The object was to ascertain the limiting proportions necessary to accelerate gelling and particularly to supply a norm for the evaluation of molecular oxygen and sulfur.

Figure 1 gives plots for various quinones; anthraquinone and xanthone are by far the most effective. Phenanthraquinone, dibenzoyl peroxide, and chloranil are less active and sulfur is least active of all. The results are calcu-

* Reprinted from the *Journal of the Society of Chemical Industry*, Vol. 64, No. 5, pages 135–138, May 1945.

lated on the basis of carbonyl or peroxidic oxygen content, thus enabling a direct comparison to be made with molecular oxygen. A recently milled, ordinary thin, air-dried crepe rubber (rubber F) was used. It is seen that 0.1–0.2 per cent of the most active agents enormously accelerates the rate of gelling and produces a firm gel in two or three hours' insolation; with larger quantities the time may be reduced to a matter of minutes, but more than 0.5 per cent on the rubber has comparatively little effect. The curves show



Hours to gel (equivalent mols of carbonyl oxygen, molecular oxygen, and sulfur)
1. Molecular oxygen. Various hydrocarbon solvents (for details see Figure 2)
2. Sulfur
3. Carbonyl oxygen as chloranil
4. Peroxide oxygen as dibenzoyl peroxide
5. Carbonyl oxygen as phenanthraquinone
6. Carbonyl oxygen as anthraquinone
7. Carbonyl oxygen as xanthone

FIG. 1.—Rates of gelling with various reagents.

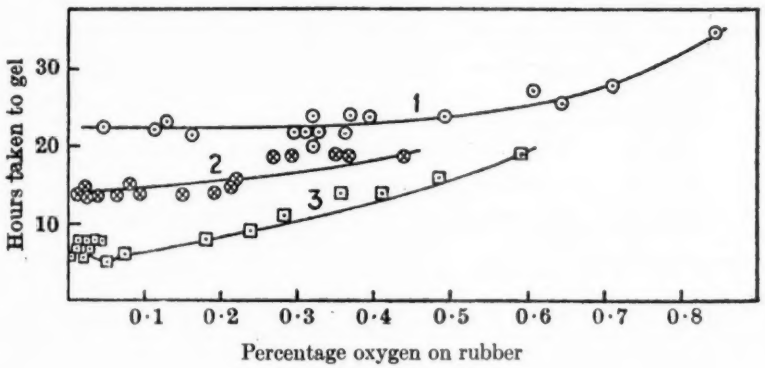
sharp inflections. The carbonyl oxygen in quinones appears to be more effective than the peroxidic oxygen in dibenzoyl peroxide. In the figure, this latter is shown at only one concentration, but other experiments confirm the relative position of benzoyl peroxide in the order of reactivity.

MOLECULAR OXYGEN AS A PHOTOGELLING AGENT

It is well known that oxygen, even in traces, may react with unsaturated compounds by activation of the olefinic double linkings, with resultant polymerization and, in the case of rubber, insolubilization and the gelling of its sols. If present in larger proportions, oxygen reacts chemically to give a variety of addition, substitution and fission products. The latter soon make themselves evident in a rubber sol when exposed to light and air by a reduction in viscosity. Molecular oxygen has therefore a two-fold action, a cross-linking or vulcanizing effect and a degradative or splitting effect. These may be

assumed to take place simultaneously. As long as sufficient oxygen is present, the degradative effect predominates, but if the source is restricted, this action ceases at a certain stage, polymerization or cross-linking sets in, and the sol gels

Rubber sols kept in tubes sealed with air so as to contain about 0.5 per cent of oxygen on the rubber, after an initial fall in viscosity and a period of many hours' exposure (during which nothing appears to happen and no recovery in viscosity takes place), gel rather suddenly; the gel is quite firm in the course of an hour or so. This may be contrasted with the behavior of a rubber sol in a tube from which substantially all the air has been removed by boiling off under reduced pressure. In this case the sol very gradually increases in viscosity until ropy and semigelled. A firm gel is seldom obtained. It seems clear that the firm gel formed in the presence of air results from the catalytic effect of the oxygen in promoting cross-linking or other form of polymerization as soon as the bulk has been absorbed in a degradative reaction; in the exhausted tube, insufficient oxygen remained to complete the polymerization, and there was no loss of viscosity since degradative oxidation was absent.



1. In various solvents. Rubber F
2. In benzene. Rubber M
3. In cyclohexane. Rubber M

FIG. 2.—Rates of gelling with molecular oxygen.

Several series of tubes containing rubber dissolved in different hydrocarbons (benzene, toluene, cyclohexane, or light petroleum) were prepared, enclosing varying volumes of air. For the smallest proportions the tubes were sealed under reduced pressure. This series included a range of from 0.00134 up to 0.848 per cent of oxygen on the rubber (0.5 gram in 10 cc. of solvent). The smaller proportions of oxygen all gave gels in 6–12 hours' insolation, according to conditions. It is noteworthy that the smallest proportions of oxygen still gave gels in the minimum time.

Some data are given in Figure 2. The upper, almost horizontal, curve represents simultaneous exposures with three different solvents. The variations with these solvents as shown in the plot are so small that all the data can be represented by the same Curve 1. The lower Curves 2 and 3 give the results of simultaneous exposures with benzene and cyclohexane, both with rubber M. These approximately horizontal curves may be contrasted with those shown by other activators, such as the quinones. Curve 1, Figure 2, is also given in Figure 1 to facilitate comparison.

SULFUR AS A PHOTOGELLING AGENT

Experiments with sulfur present some difficulty, for, after a time, a deposit forms on the wall facing the sun. This occurs both with sulfur dissolved in benzene and with sulfur vapor in an exhausted tube. It appears to form independently of the rubber and, being opaque, hinders gelation.

The quantities of sulfur which combine with rubber under the influence of light may be considerable. In the presence of 3 per cent of sulfur, 1–2 per cent of combined sulfur is obtained in 30–60 hours' exposure, but the physical properties as judged by handle are inferior to those of a vulcanizate with this percentage of combined sulfur obtained thermally. It may be that overcure takes place photochemically with a smaller proportion of combined sulfur. With a greater excess of sulfur, *e.g.*, 10 per cent, combined sulfur in the dry gel may exceed 3 per cent.

The hydrocarbon used as a solvent has little or no effect on rate of combination with sulfur (Table I), but the time taken to gel varies.

TABLE I

VARIOUS HYDROCARBON SOLVENTS WITH 10 PER CENT OF SULFUR ON THE RUBBER EXPOSED CONCURRENTLY FOR 30 HOURS' DIRECT SUNSHINE

Solvent	Hours taken to gel	Percentage combined S
Benzene	15	2.26
Toluene	15	2.78
m-Xylene	*30+	1.33
o-Xylene	6	2.18
p-Xylene	4.5	2.25
Mesitylene	*30+	2.20
Light petroleum (b.p. 60–80°)	7	2.25

* Incompletely gelled after 30 hours.

Gelling with *m*-xylene as solvent, whether the process is activated with sulfur or oxygen, is always slow and incomplete. Thermal vulcanization accelerators do not promote or accelerate gelling in the presence of sulfur, nor do they increase the percentage of combined sulfur, even in the presence of zinc stearate. The accelerators used were of necessity restricted to those having no thermal action at the maximum temperature of exposure, which did not exceed 60°. Parallel experiments with dry rubber, flowers of sulfur, and thermal accelerators rubbed on to the surface gave similar results[3]. Curve 2, Figure 1, is the left-hand portion of a curve showing the effect of the proportion of sulfur used on the rate of gelling. One-half per cent on the rubber is the approximate minimum required to give complete gelation. Consequently the curve at this point tends upwards as indicated by the broken line. With 2–3 per cent of sulfur the solution gels easily, but larger quantities up to 10 per cent have very little further accelerating action, and the curve becomes substantially horizontal. In a series of parallel experiments with benzene, cyclohexane, and light petroleum, and with varying quantities of sulfur (Table II), the effects of diminishing proportions of sulfur are shown. The smaller proportions of sulfur, insufficient to produce a firm gel, give increased viscosity or ropy masses. The figures in Table II, as in Table I, indicate that the solvent is without influence on the proportions of sulfur which combine, but does influence the rate of gelling. The solubility and swelling properties of the gel run parallel with the combined sulfur. With the maximum proportion of sulfur the gels produced appear well vulcanized, and could be described as

benzene-insoluble. With the smallest proportions of sulfur, enormously swollen gels were obtained which, however, did not disperse unless shaken and then incompletely. Generally the rate of gelling or change of viscosity was irregular and difficult to estimate.

TABLE II

VARYING PROPORTIONS OF SULFUR WITH THREE HYDROCARBON SOLVENTS. TOTAL EXPOSURE 30 HOURS' DIRECT SUNLIGHT

Sulfur added (%)	Sulfur combined			Hours to gel			Swelling index*	Proportion soluble*
	Benzene	Cyclohexane	Petroleum	Benzene	Cyclohexane	Petroleum	Gels formed in light petroleum	
3.00	1.56	1.49	1.46	4	14	22	12.6	0.08
0.5	0.39	0.39	0.43	30	30+	30+	34.8	0.33
0.25	0.24	0.11	0.25	30+	30+	30+	68.5	0.37
0.10	0.07	0.07	0.08	30+	30+	30+	82.5	0.45
0.05	0.05	0.04	0.05	30+	30+	30+	—	—
Nil	—	—	—	30+	30+	26	—	—

* The "swelling index" is the volume of a unit weight of insoluble rubber at maximum swelling and the "proportion soluble" is the soluble residue of a unit weight of rubber after solvent treatment.

Combined sulfur was determined after all the tubes had been insolated for 30 hours. Allowance was made for sulfur naturally present (about 0.03 per cent), as shown by analysis of the controls.

VARIATIONS IN THE RUBBER

It has previously been observed that extraction with acetone has no appreciable effect on rate of gelling, but some small variations were specific to the rubber. These observations applied mainly to fast-gelling sols. With inert hydrocarbons as solvents, the source and purification of rubber have been found to modify appreciably the rate of gelling. Rubber M was a low-nitrogen, estate-prepared crepe, and gelled appreciably faster than the ordinary thin crepe F, milled to substantially the same degree. A Sumatra "sole crepe", similarly milled, gelled at about the same rate as F, so that the purification process which was applied to the rubber in latex form may be the cause of the higher rate of gelling.

EXPERIMENTAL

The hydrocarbon solvents were used as purchased from B.D.H., except *m*-xylene, which was prepared from commercial xylene. The few per cent of *o*- and *p*-xylene were removed by preferential oxidation with nitric acid[4], distillation in steam, and rectification. This purification had no effect on the rate of gelling of rubber sols made with the solvent.

The general procedure was, as follows. One-half gram of recently milled crepe rubber was placed at the bottom of a $6 \times \frac{7}{8}$ inch test-tube, with wall 0.5 mm. thick. The tubes were constricted to give varying capacity of 10–25 cc. as the experiment required. In the experiments with activators, 11 cc. of solvent was introduced by a capillary funnel, and the activator was dissolved in the solvent used. The tube was then exhausted so that the solvent boiled for two minutes. This left approximately 10 cc. of solvent in the tube, which was then sealed off. The rubber was dissolved by shaking at intervals in darkness. Dissolution was usually complete in one or two days. The tubes for each series, numbering perhaps twenty at a time, were exposed alongside

one another in a slanting rack, no part of the tube being obscured. The racks were exposed as a rule in summer only, to give not more than five hours' effective insolation in the middle of the day. The racks were shifted from time to time to preserve a perpendicular incidence of the light as far as practicable. Repeat tests usually showed fair concordance, but no conclusions were drawn except from series insolated simultaneously.

The solvent swelling test was carried out by immersing 0.1 gram in 10 cc. of benzene in corked tared test-tubes in darkness for three days; the benzene was then decanted, replaced, and the tube set aside in the dark for a further seven days, after which the benzene was poured off as completely as possible and the sides of the tube and surface of the gel (when firm enough) dried with a plug of cotton wool on a wire large enough to fill the tube. After weighing the gel, the benzene was removed slowly by exposure to the air and the removal completed in a water-oven until the weight was constant.

DISCUSSION

In a recent paper[5] Naunton endeavored to show that photogels could not be produced in complete absence of oxygen, but in spite of every precaution, beginning with latex saturated with nitrogen, coagulated, and further treated out of contact with air, the solution obtained gelled in 3 hours, whereas a similar solution with free access of air took 16 hours. The delay in the latter case is presumably due to the degradative effect of the oxygen enclosed with the rubber, so that gelling did not take place until this was almost completely absorbed. It is, however, not easy to explain gelling in the former case, in which the oxygen was so carefully excluded.

In spite of this negative result, it still appears probable that the presence of oxygen or some other catalyst is necessary because of certain limited proportion of air is essential (in the absence of other catalysts) if a firm gel is to be obtained; the range so far ascertained includes proportions from as low as about 0.001 per cent on the rubber, up to nearly 1 per cent, although the time taken to form a gel is longer with the higher proportions. When the oxygen present is reduced to the smallest possible proportions by boiling out part of the solvent under reduced pressure, there is generally insufficient remaining to produce a firm gel, although there is always some increase in viscosity and eventual ropiness.

The proportion of oxygen necessary to produce a firm gel must be very small indeed, as indicated by the curves (Figure 2). These are flat and show hardly any indication of an upward turn as they approach the y-axis. It seems that, on insolation, the time taken to oxidize the rubber before cross-linking becomes evident grows less and less as the air content is correspondingly reduced, and becomes almost constant when only 0.1 or 0.2 per cent of oxygen on the rubber remains. If the proportion of oxygen is increased beyond the limit of the graph, the curves tend upwards, and become eventually vertical when the limiting figure is reached at which oxidation proceeds but gelling never takes place. Some idea of the minimum of oxygen necessary might be obtained from experiments with tubes exhausted by boiling off the solvent, if the solubility of oxygen in raw milled rubber were known, as this is the probable source of oxygen in the tubes. There are no direct data, but it has been stated that the amount which dissolves in raw rubber is much the same as in vulcanized rubber[6] and is estimated at 15–16 cc. per 100 g., *i.e.*, about 0.02 per cent by weight[7]; this is a much higher figure than that found to be necessary

to produce a firm gel. Rubber increases in weight on milling under ordinary conditions by 0.04–0.1 per cent[8]; this again is too high a figure. It is probable that the peroxides first formed during milling decay quickly and that their products have no activating effect.

The lower limit of oxygen so far found necessary for the formation of a gel, approximately 1 : 100,000 by weight, indicates that one atom of oxygen induces sufficient cross-linkages to gel a 5 per cent solution containing 23,600 C_5H_8 units, assuming that two atoms of oxygen are required for linking two rubber molecules. Since it has been estimated[9] that the average degree of polymerization of milled crepe is approximately 370, it follows that the linking of one in every 64 molecules is sufficient to convert a 5 per cent sol into gel consistency. If, however, the molecules are directly linked without intervention of oxygen atoms, the oxygen functioning as the start of a chain reaction, a very much larger proportion of the rubber molecules may be cross-linked. This latter view is the more probable when regard is taken for the high efficiency of many quinones and other carbonyl compounds.

The literature in regard to sulfur as an activator is contradictory. Porritt[10] states that sulfur prevents gelation. Naunton found a slight increase in viscosity, but gelation could not be obtained, although the sols were exposed for several months to summer sunlight (*loc. cit.*). Stevens arrived at a contrary conclusion[11]. Here again observations are difficult to reconcile with the results recorded in this paper and many repeats of these, unless it be that the opaque deposit which forms on the walls of the tube is sometimes accountable for failure to obtain a gel, but this deposit does not usually appear until some hours after the initial exposure.

Attention may be drawn to the parallel vulcanization of dry rubber and rubber sols when insolated both with and without activators. Stress-strain curves exactly resembling those for slightly vulcanized rubber were obtained[3] by exposing sheets of milled rubber about 0.1 mm. thick in evacuated tubes. In this way a breaking load of over 20 kg. per sq. cm. has been obtained with an extension of 800 per cent. Probably a trace of air in the tubes provided the activator, although the mode of cross-linking is uncertain. Similarly, photovulcanization of rubber in the solid state may be obtained with sulfur and the various quinones in the form of powder applied to the surface of the rubber sheet. Some of these reagents are so active in linking the molecules that a physically improved product can be obtained, even in the presence of air. It would be expected, therefore, that vulcanization on parallel lines would take place in rubber sols, resulting in insolubilization and consequent separation of the rubber as a gel similar in properties to that produced by a little sulfur chloride in the cold.

The photovulcanization of rubber, either solid or in solution, by minute quantities of oxygen has no parallel in thermal vulcanization. Milled rubber as "cut sheet" was found to be substantially unaltered, and certainly unvulcanized, after heating in evacuated tubes for varying periods in the dark at temperatures not exceeding the maximum reached during insolation (60°). Thermal vulcanization with benzoyl peroxide requires more of the reagent than the photochemical process. Using 10 per cent thermally, some 3.5 per cent combines with rubber, no doubt accounting for the rapid aging (physical deterioration) of the vulcanized product[12]. This is not observed with photochemical vulcanization, in which very much smaller proportions of reagent are used. Similarly, much larger proportions of quinones and chlorinated quinones are required thermally than photochemically. On the other hand, sulfur is

effective on much the same scale thermally as photochemically if the reaction is measured by the amount of sulfur which combines with the rubber. Remembering also that there is no correspondence between combined sulfur and tensile or elastic properties unless the conditions are kept constant, that is, nature and amount of accelerator, etc., the conclusion is reached that vulcanization as measured by physical change (tensile properties) is independent of the reaction of the sulfur or other reagent with the rubber. Indeed, there is evidence that this reaction should be kept at a minimum to obtain the best tensile and elastic vulcanizates. Boggs and Blake[13] state that any combined sulfur in excess of 0.5 per cent is detrimental. Somerville and Russel[14] obtained excellent vulcanizates with as little as 0.3 per cent of combined sulfur. The figure depends, no doubt, on vulcanizing at the lowest possible temperature in the shortest possible time. This is known to be the case for photochemically vulcanized rubber, and it is desirable to reduce the oxygen to the smallest proportion possible. The proportion required is so small that the oxygen is scarcely sufficient to bridge the chains; consequently, its action is purely catalytic in bringing about the direct linking of the molecules. Similar considerations apply to sulfur vulcanization, although it seems more difficult to effect this with very small percentages of sulfur, oxygen being far more powerful as a vulcanizing agent, at least photochemically.

SUMMARY

This paper details an evaluation of a number of rubber photogelling agents or activators under insolation, particularly oxygen and sulfur. Contrary to previous statements, both elements are shown to be activators, and sulfur combines with rubber as in thermal vulcanization. Molecular oxygen, after allowing for degradative oxidation, is an extremely powerful gelling agent, comparable with quinonic or peroxidic oxygen.

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THE VULCANIZATION OF RUBBER WITH PHENOL FORMALDEHYDE DERIVATIVES. I*

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INTRODUCTION

As is generally known, rubber can be vulcanized not only by sulfur, but also by a large number of other agents. Although sulfur is still regarded as the vulcanizing agent par excellence, yet it has certain drawbacks, which may be illustrated as follows. On vulcanization with sulfur, products are formed which always have a certain similarity of structure, independent of the composition of the original mixtures. To vary the properties of the vulcanized products, a number of special substances, such as fillers, accelerators, antioxidants and the like, have to be added. Since in practice, however, rubber is subject to a great variety of requirements, such as high resistance to heat, abrasion and oils, a better impermeability for gases, special electrical properties, etc., it is highly important that vulcanizates should be produced with widely divergent properties. However, in vulcanization with sulfur, only variations on the same theme are obtained.

It is obvious that there is only one possibility of meeting these difficulties, namely, by the employment of other vulcanizing materials. Among the large numbers of these agents which have been tried up to now, the phenol-formaldehyde resins emerge as the most useful. These resins have several advantages as vulcanizing materials, the most important of which are as follows:

1. Phenol-formaldehyde resins react chemically with rubber to form vulcanizates and harden simultaneously. In this way it is possible to combine rubber and resin in the most useful manner, providing that hardening and vulcanization take place at the same time.

2. The number of phenol-formaldehyde resins is already very large and can be extended if desirable. Consequently a great many of the most varied resins can be applied and the properties of the products studied.

3. The addition of special agents such as antioxidants, accelerators and the like, will be superfluous, for it is possible to introduce them as different groups in the original phenols or resols.

4. Phenol-formaldehyde resins have proved to be most useful materials from a technical point of view, so it may be expected that a combination with rubber will also lead to products of practical value.

A great deal of research has already been carried out in the field of synthetic resin-rubber combinations, but most of these investigations have been performed without any scientific insight into the subject[1]. It is, therefore, not surprising that no combination of great practical value has been found until recently. Only a few years ago the first scientific investigations were carried out, attention being devoted to the formation of real chemical bonds between

* Reprinted from the *Recueil des Travaux Chimiques des Pays-Bas*, Vol. 63, No. 4, pages 147–169, April 1944. This investigation is described in detail also in the Thesis of van der Meer, entitled "De Vulcanisatie van Rubber met Phenol-Formaldehyd Derivaten", Delft, Holland, 1943. The present paper represents Communication No. 47 of the Plastics Department of the Rubber Foundation.

rubber and resins[2]. Many problems, however, were still connected with this reaction mechanism. Therefore it is important to extend that branch of research and to attempt to elucidate the reaction mechanism between rubber and phenol-formaldehyde resins.

DEVELOPMENT OF THE INVESTIGATION ON VULCANIZING SYNTHETIC RESINS

In 1939, at the start of the investigation of vulcanization by synthetic resins, only very little information was available. Wildschut[3] had vulcanized rubber with a few commercial synthetic resins of the phenol-formaldehyde type, and had described a vulcanizing resin prepared from pentaphen (*p*-tertio-amylphenol) and formaldehyde. Thus it had been proved possible to vulcanize rubber with phenol-formaldehyde resins.

Our investigation started with the preparation of some resins from ordinary phenol, formaldehyde and sodium hydroxide in the usual way, followed by an attempt to combine the resols obtained with several higher alcohols to induce benzene solubility[4]. It was expected that these resols would vulcanize rubber because of their thermosetting qualities and solubility in benzene. Entirely different results were obtained, however, as these resols proved totally insoluble in benzene. On treatment with the higher alcohols, carried out by heating mixtures of resols and alcohols for 5–6 hours at about 100° C, the resols did not combine, but were hardened to a considerable extent. These unfavorable results were not improved by varying the ratio of the reacting compounds, the temperature, the time, the nature of the alkali, etc.

Consequently another phenol had to be taken as a starting material. Therefore similar experiments were carried out with *m*-cresol, which also has three reaction-favorable positions and is thus able to produce a three-dimensional net structure. Moreover *m*-cresol is one of the most highly reactive phenols known in the synthetic resin industry. The results, however, were altogether identical with those from ordinary phenol, in this case also the hardening reaction taking place too rapidly. For that reason it was necessary to reduce the rate of hardening by starting from a phenol having only two reaction-favorable positions. Experiments carried out with *p*-cresol immediately yielded good results.

TABLE I

MECHANICAL PROPERTIES OF A VULCANIZATE (SCHOPPER RINGS) OF 100 PARTS OF RUBBER AND 40 PARTS OF RESIN I

Tensile strength (kg. per sq. cm.)	44
Elongation at break (percentage)	631
Permanent set *	12—5
Hardness (Shore Durometer A)	36

* The rubber is stretched for 24 hours to 200 per cent, then released, and the permanent set measured after 1 hour.

A solution of 1 mole of *p*-cresol, 2 moles of formaldehyde and a small amount of ammonia as a catalyst, was kept for 16 hours at 20° C and subsequently 6½ hours at 70° C. The resol which separated was heated with 1 mole of tert.-amyl alcohol for 13 hours at 112–114° C, and yielded a yellow, solid resin (I), soluble in benzene.

A mixture of 100 parts of rubber and 40 parts of the resin I, heated for 2 hours in a press between parallel plates at 155° C, yielded a vulcanizate with the properties shown in Table I.

It was remarkable that with a variety of alcohols similarly good results were obtained, the influence of the nature of the alcohols being of only minor importance. Treating 2,6-dihydroxymethyl-4-methylphenol[5], the base compound of the resols in question with higher alcohols, also yielded analogous results. From the observation that resols derived from ordinary phenol and *m*-cresol did not produce any serviceable products when treated with higher alcohols, it could be expected that also in the case of the *p*-cresol derivatives no important chemical changes had been brought about by the alcohols. Consequently an attempt was made to vulcanize rubber with resols, without any preliminary treatment in the manner described. It was not surprising that in these last cases vulcanization could indeed be achieved. But then the vulcanizing properties of 2,6-dihydroxymethyl-4-methylphenol itself had also to be investigated. These experiments also yielded positive results, and the mechanical properties of vulcanizates of this type are shown in Table II.

TABLE II

MECHANICAL PROPERTIES OF VULCANIZATES (SCHOPPER RINGS) OF 100 PARTS OF RUBBER AND 30 AND 40 PARTS OF 2,6-DIHYDROXYMETHYL-4-METHYLPHENOL, RESPECTIVELY. VULCANIZATION TIME, 2 HOURS, AT 155° C

	30 parts	40 parts
Tensile strength (kg. per sq. cm.)	139	159
Elongation at break (percentage)	552	513
Modulus at 100% (kg. per sq. cm.)	9	10
Modulus at 200%	14	20
Modulus at 400%	56	82
Hardness (Shore A)	40	45

At first it was not clear why resols derived from *p*-cresol had vulcanizing properties, whereas those from ordinary phenol and *m*-cresol had not. In the hope of solving this problem, 51 different phenols were investigated, including those with one and with two nuclei, mono- and divalent phenols with none, one, two and three substituents, etc. Generally, nine resols were prepared from each phenol in the following manner:

1 mole of phenol and 1.25 moles of sodium hydroxide were heated in a dilute solution (10 g. phenol in 0.5 l. water) at 70° C with 2, 4 and 8 moles of formaldehyde (33% solution), respectively, each separate mixture for 32, 64 and 128 hours. After acidification with 4 *N* acetic acid, the resols obtained were washed with water and dried.

The resols obtained in this way showed great differences in their condensation stages. Because of this there was little chance of missing any vulcanizing properties on carrying out the vulcanizing test as already described above.

A number of phenol-dialcohols were also prepared, derived from phenols with two reaction-favorable positions. As a rule the preparations were carried out as described in the case of 2,6-dihydroxymethyl-4-methylphenol. Table III shows these compounds, all of which were tested for vulcanizing properties at a temperature of 155° C in the usual way.

From these investigations with resols and phenol-dialcohols a general rule could be deduced. It was found that, with only one exception, all resols and phenol-dialcohols with which rubber could be vulcanized were derived from phenols possessing two reaction-favorable positions. The converse, that all phenols with two reaction-favorable positions always yielded resols with vul-

canizing properties, appeared not to be true. As examples of these exceptions may be mentioned resols derived from *o*-cresol, guaiacol, *o*- and *p*-aminophenol, *p*-cyanophenol, *p*-rhodanophenol, salicylic acid, 2,5-xylenol, 3,5-dichloro-4-cyanophenol and all polyvalent phenols with the hydroxyl groups in one nucleus. Of the phenol-dialcohols, only 4,6-dihydroxymethyl-2-methylphenol and 4,6-dihydroxymethyl-2-chlorophenol did not show any vulcanizing properties at 155° C. Several of these exceptions could easily be explained by the fact that the phenols in question reacted so violently with formaldehyde that

TABLE III

PHENOL-DIALCOHOLS, TESTED FOR VULCANIZING PROPERTIES AT 155° C

Name	Melting point ° C	Vulcanization
1. 4,6-Dihydroxymethyl-2-methylphenol[6]	94	−
2. 2,6-Dihydroxymethyl-4-methylphenol[5]	130	+
3. 2,6-Dihydroxymethyl-4-ethylphenol[7]	86–87	+
4. 2,6-Dihydroxymethyl-4-propylphenol[7]	88–89	+
5. 2,6-Dihydroxymethyl-4-isopropylphenol	125–127	+
6. 4,6-Dihydroxymethyl-2-tertiobutylphenol[8]	97–97.5	+
7. 2,6-Dihydroxymethyl-4-cyclohexylphenol[9]	103.5–104	+
8. 2,6-Dihydroxymethyl-4-phenylphenol[9]	113–114	+
9. 2,6-Dihydroxymethyl-4-methoxyphenol[10]	127	+
10. 4,6-Dihydroxymethyl-2-chlorophenol[11]	117.5–119	−
11. 2,6-Dihydroxymethyl-4-chlorophenol[10]	153–154	+
12. 2,6-Dihydroxymethyl-3-methyl-4-chlorophenol[12]	135–136	+
13. 2,6-Dihydroxymethyl-3,4,5-trichlorophenol[7]	146–147	+
14. Bis-(2-hydroxy-3-hydroxymethyl-5-methylphenyl)-methane[13]	147–148	+
15. 1-Hydroxy-2,6-bis-(2-hydroxy-3-hydroxymethyl-5-methylbenzyl)-4-methyl-benzene[13]	>190 decomposition	+

The signs + and − indicate positive and negative vulcanization reactions.

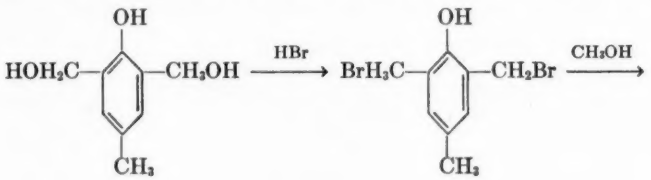
Compounds 3, 4, 5, 6 and 13 were prepared at the Organic Chemical Laboratory of the State University at Groningen.

almost immediately insoluble resites were obtained (aminophenols, *p*-rhodanophenol, some polyvalent phenols, as resorcinol, etc.), whereas other phenols did not react or only to a very slight extent (*p*-cyanophenol, nitrophenols). Neither could a reaction with rubber be observed when too many polar groups were present, for this caused insolubility in benzene.

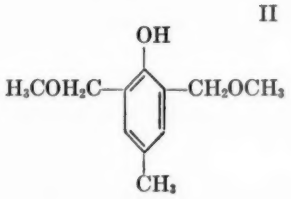
The explanation of the behavior of *o*-cresol and its homologs proved far more difficult. From that phenol, different resols as well as the dialcohol[14] could easily be prepared, but none of these derivatives possessed any vulcanizing power. The solution of this problem was not found until the mechanism of the vulcanization reaction of the phenol-formaldehyde derivatives had been elucidated. Then it could be deduced from a theoretical point of view that in this case the vulcanization reaction should take place at a higher temperature, 200° C, for instance. This supposition was afterwards tested experimentally. Details will be given in Part II.

It was not clear why treatment of the resols with the higher alcohols mentioned had so little influence on their vulcanizing properties, although the possibility remained that no chemical reaction between the two substances had taken place. To obtain with certainty such a chemical reaction in the case

of a simple alcohol, 2,6-dihydroxymethyl-4-methylphenol was treated with methyl alcohol in an indirect way, as is shown in the following formulas:



I II



III

This compound 2,6-dimethoxymethyl-4-methylphenol[12] (III), which was derived from 2,6-dihydroxymethyl-4-methylphenol (I) via 2,6-dibromomethyl-4-methylphenol[15] (II), however, did not show any vulcanizing power. From this it appeared very probable that in the former experiments no chemical reaction between resols and alcohols took place, as in those cases, in contrast with the example formulated, practically no influence of the alcohols on the vulcanizing properties could be observed.

Vulcanization experiments were also carried out with the bromo compound (II), which was unexpectedly found to be the most rapidly working vulcanizing agent of all the substances examined. Some results obtained with this compound are given in Table IV.

TABLE IV

MECHANICAL PROPERTIES OF VULCANIZATES OF 100 PARTS OF RUBBER AND 10 PARTS OF 2,6-DIBROMOMETHYL-4-METHYLPHENOL. VULCANIZATION TIME, 30 MINUTES

Vulcanization temperature (° C)	120°	125°
Tensile strength (kg. per sq. cm.)	51	90
Elongation at break (percentage)	665	695
Modulus at 100% (kg. per sq. cm.)	3	3
Modulus at 200%	6	6
Modulus at 400%	12	16
Hardness (Shore Type A)	28	30

From these experiments it was clear that the vulcanizing properties observed with the phenol-dialcohols were present in this halogen compound to a far more pronounced degree. Subsequently other halogen compounds, a survey of which is given in Table V, were also examined, all yielding similar results.

To find the cause of the vulcanizing properties of the phenol-formaldehyde derivatives, it was obvious that these halogen compounds should be investigated especially. Being insoluble in alkali, although possessing phenolic hydroxyl groups, they had to be classified as pseudo-phenol halides, which are closely related to the methylene quinones[19]. This fact suggested the idea that, in vulcanizing rubber with the said halogen compounds, and probably also with phenol-dialcohols and resols, methylene quinones might be formed

TABLE V

HALOGEN DERIVATIVES OF PHENOL-DIALCOHOLS, SHOWING VULCANIZING PROPERTIES

Name	Melting point °C
1. 2,6-Dibromomethyl-4-methylphenol[15]	115–117
2. 2,6-Dibromomethyl-3-bromo-4-methylphenol[12]	95–96
3. 2,6-Dibromomethyl-3,5-dibromo-4-methylphenol[16]	149–150
4. 4,6-Dibromomethyl-2-methylphenol[12]	109.5–110.5
5. 2,6-Dichloromethyl-4-methylphenol[17]	87
6. 2,6-Dichloromethyl-4-chlorophenol[12]	90–91
7. 2,6-Dichloromethyl-3,4,5-trichlorophenol[18]	84–85.5

These compounds show optimum vulcanizing power after 10–30 minutes at a temperature of 120–125° C.

as intermediates in the vulcanization process. Starting from this supposition, a theory was developed by which all the phenomena observed could be explained and others predicted.

THE METHYLENE QUINONE THEORY OF THE VULCANIZATION PROCESS

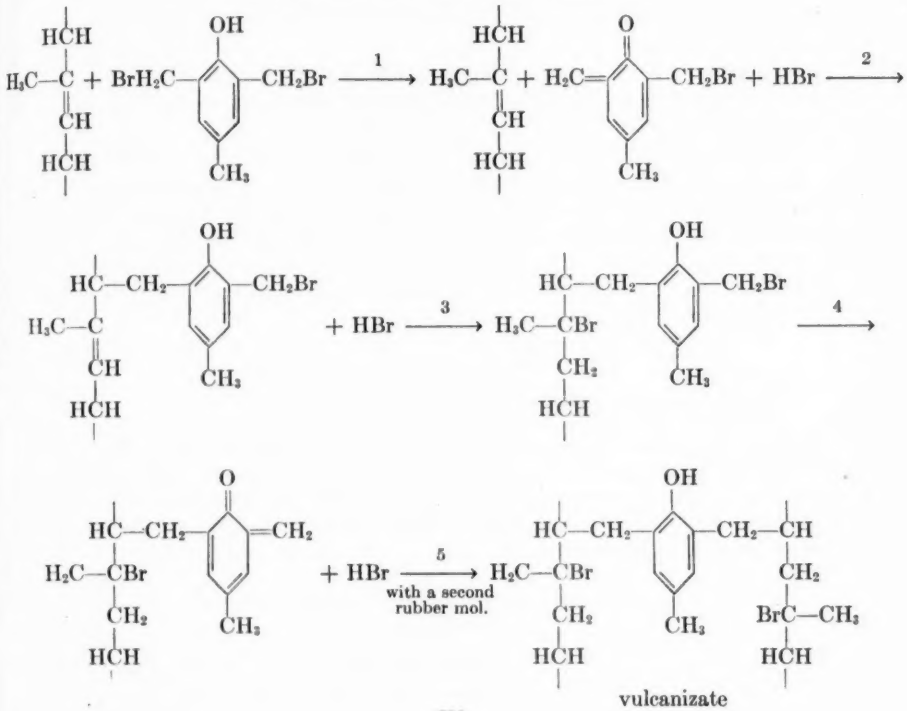
To explain the vulcanization mechanism of the phenol-formaldehyde derivatives, the formation of bridge linkages between the rubber molecules must be considered as an essential part of the process[20]. Thus in the present case a mechanism has to be found by which vulcanization can be explained from that point of view.

A theory, based on that principle already mentioned in the preceding paragraph, is demonstrated in the following formulas (IV), choosing 2,6-dibromomethyl-4-methylphenol as the vulcanizing agent.

This bromo compound has only little stability, and it decomposes when heated above its melting point (116° C), with liberation of gaseous hydrogen bromide and formation of a resin. When heated in solution, as during vulcanization, hydrogen bromide is liberated and a very reactive methylene quinone is formed (Reaction 1). This methylene quinone reacts easily with "active" hydrogen atoms, forming an addition compound. In the rubber molecule such active hydrogen atoms are present in the CH_2 groups (allyl configuration). One of these active hydrogen atoms combines with the oxygen atom of the methylene quinone; the rest of the rubber molecule combines with the methylene group (Reaction 2). At the same time the hydrogen bromide is added to a double bond of the rubber (Reaction 3). For simplicity this addition is supposed to occur at the neighboring double bond. When these reactions are finished, a methylene quinone can be formed once more, as for the second time a phenolic hydroxyl group and an *o*-bromomethyl group are present in the molecule. Thus hydrogen bromide is again liberated and a methylene quinone derivative of rubber is formed (Reaction 4). Then Reactions 2 and 3 are repeated, this time with a second rubber molecule (Reaction 5). In this way a bridge linkage between two rubber molecules is formed, in other words: a vulcanizate.

The pairs of active hydrogen atoms in the rubber molecule have different reactivities in consequence of the asymmetrical structure of the isoprene units. It is not known which of the two has the greater reactivity, but in Reaction IV the first rubber molecule is supposed to react in one way, the second in the other. This supposition is, however, not important with regard to the further development of the hypothesis mentioned above.

REACTION SCHEME OF THE VULCANIZATION PROCESS OF RUBBER WITH 2,6-DIBROMOMETHYL-4-METHYLPHENOL



IV

The addition of hydrogen bromide to the double bonds of rubber molecules must be considered as a side reaction. This can immediately be concluded from the fact that 2,6-dihydroxymethyl-4-methylphenol, from which the halogen compound is derived, also has very good vulcanizing properties. Vulcanization with this compound can be formulated similarly, water instead of hydrogen halide being liberated in this case. As water does not react with double bonds in the rubber molecules, the former remain in the vulcanizates.

Summarizing, it may be concluded that the vulcanization reaction between rubber and 2,6-dibromomethyl-4-methylphenol can be formulated best as shown in Scheme IV. In a following article further supporting arguments for this methylene quinone theory will be given.

EXPERIMENTAL PART

2,6-DIHYDROXYMETHYL-3-METHYL-4-CHLOROPHENOL

To a solution of 142.5 g. of 3-methyl-4-chlorophenol and 50 g. of sodium hydroxide in 186 cc. of water, 212 cc. of a 33% solution of formaldehyde was added and this mixture kept at room temperature for 7 days. The crystallized sodium salt of the phenol-dialcohol was filtered by suction, washed with a solution of sodium chloride and dissolved in water. After acidification with 313 cc. of 4 *N* acetic acid, the dialcohol was precipitated, filtered, washed with

water, dried, and recrystallized from a mixture of ethyl acetate and petroleum ether (boiling at 40–60° C). White crystals, melting at 135–136° C with decomposition. Yield 91 g. = 45%.

Analysis:

Found:	C 53.29; H 5.37; Cl 17.58.
Calculated for $C_9H_{11}O_3Cl$(202.39):	C 53.34; H 5.44; Cl 17.51.

2,6-DIMETHOXYMETHYL-4-METHYLPHENOL

1.74 cc. of pyridine was added to a solution of 2.94 g. of 2,6-dibromomethyl-4-methylphenol in 9 cc. of absolute methyl alcohol, and this mixture boiled for 13 hours. After the methyl alcohol was distilled off, the residue was treated with water and benzene. The benzene extract was washed with water, dried and fractionated. A colorless liquid was obtained, boiling at 100–102° C and 0.2 mm. pressure. Yield 0.54 g. = 24%.

Analysis:

Found:	C 67.16, 67.25; H 8.01, 8.05.
Calculated for $C_{11}H_{16}O_3$(195.93):	C 67.33; H 8.17.

Afterwards, when the great reactivity of the pseudophenol halides was better known, these compounds appeared to react very easily with water and alcohols, forming the corresponding dihydroxy and dialkoxy derivatives, also without the aid of an alkaline agent. Therefore the addition of pyridine described above could be omitted.

2,6-DIBROMOMETHYL-3-BROMO-4-METHYLPHENOL

1.5 cc. of bromine was added to a solution of 2 g. of 2,6-dibromomethyl-4-methylphenol in 12 cc. of carbon tetrachloride. After keeping this mixture in the dark at room temperature for 3 days, the solvent and the excess of bromine were evaporated and the residue recrystallized 5 times from petroleum ether (boiling at 80–100° C), using charcoal as a decolorizing agent. White needles, melting at 95–96° C. Yield 0.75 g. = 30%.

Analysis:

Found:	C 28.88; H 2.49; Br 65.29.
Calculated for $C_9H_9OBr_3$(372.65):	C 28.97; H 2.52; Br 64.32.

Although the bromine values do not correspond as well as could be desired, still this method of bromination may be considered to supply only 1 atom of bromine in the molecule. The constitution could be proved by a further bromination of the compounds, yielding the well-known 2,6-dibromomethyl-3,5-dibromo-4-methylphenol[16], melting at 149–150° C. A mixture of this and the compound obtained directly by bromination of 2,6-dibromomethyl-4-methylphenol according to the literature was found to melt at the same temperature.

4,6-DIBROMOMETHYL-2-METHYLPHENOL

50 g. of 4,6-dihydroxymethyl-2-methylphenol was dissolved in 150 cc. of glacial acetic acid saturated with dry gaseous hydrogen bromide. This red solution was saturated with dry hydrogen bromide once more, after which the desired halogen compound crystallized out. The mixture was cooled to 0° C and filtered by suction through a glass funnel, the crystals dried over calcium chloride and solid sodium hydroxide and subsequently recrystallized from

petroleum ether (boiling at 80–100° C), using charcoal for decolorizing purposes. White needles, melting at 109.5–110.5° C. Yield 51 g. = 58%.

Analysis:

Found:	C 37.12; H 3.47; Br 54.94; 54.96.
Calculated for $C_9H_{10}OBr_2$(293.75):	C 36.75; H 3.41; Br 54.40.

2,6-DICHLOROMETHYL-4-CHLOROPHENOL

A mixture of 66 g. of 2,6-dihydroxymethyl-4-chlorophenol and 200 cc. of glacial acetic acid was saturated with dry gaseous hydrogen chloride at room temperature. The compound soon crystallized, and it was recrystallized from petroleum ether (boiling at 40–60° C). White needles, melting at 90–91° C. Yield 24 g. = 30%.

Analysis:

Found:	C 42.60; H 3.23; Cl 47.27.
Calculated for $C_8H_7OCl_3$(225.29):	C 42.59; H 3.11; Cl 47.20.

A far better yield was obtained in the following way: 25 cc. of thionyl chloride were added to a suspension of 10 g. of 2,6-dihydroxymethyl-4-chlorophenol in 85 cc. of chloroform, whereupon the mixture was boiled until the development of gas had ceased. Then the excess of thionyl chloride and the solvent were distilled off under reduced pressure and the residue recrystallized from petroleum ether. Melting point 89–90° C. Yield 9.1 g. = 76%. The melting point of a mixture with the compound synthesized in the previous manner, showed no depression.

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II

COMPARISON OF THE VULCANIZING PROPERTIES OF PHENOL-DIALCOHOLS AND THEIR HALOGEN DERIVATIVES

In Part I it was stated that, in vulcanizing rubber with phenol-formaldehyde derivatives, methylene quinones act as intermediates. Although the formation of these compounds is characteristic of pseudophenol halides, it is not necessary that the vulcanizing agents possess a similar character. This fact is proved by the behavior of phenol-dialcohols, for these substances combine vulcanizing properties with solubility in alkalies. These compounds are also capable of producing methylene quinones, but at a higher temperature,

since the liberation of water does not take place so easily as the liberation of hydrogen halide from the pseudophenol halides. Thus a relation between the stability of the vulcanizing agents and their rate of vulcanization can be established. Comparing the compounds 4,6-dihydroxymethyl-2-methylphenol and 2,6-dihydroxymethyl-4-methylphenol, 2,6-dichloromethyl- and 2,6-dibromomethyl-4-methylphenol, which show a decreasing stability in that sequence, an increasing rate of vulcanization can be observed. Thus in this respect the phenol-dialcohols behave with rubber in a way analogous to that of their halogen derivatives; only the temperature required to obtain the same effect is higher.

On the other hand, there are also important differences between the vulcanizing properties of the two kinds of compounds. In vulcanizing rubber with pseudophenol halides, the two primarily formed reaction products, hydrogen halide and methylene quinone, combine spontaneously with rubber, resulting in a rapid progress of the reaction. If these halogen compounds are heated without rubber, the reaction products remain for a certain time in the mixture, and cause a decrease of the reaction rate. In consequence, there must be a comparatively great difference between their temperatures of decomposition and vulcanization, the latter being considerably lower. In fact it is possible to vulcanize with these substances within 15 minutes at a temperature of 100° C, whereas the chloride derivative shows a decomposition temperature of about 130–140° C, and the bromine compound several degrees above its melting point at 115–117° C.

Since, during vulcanization, the phenol-dialcohols liberate water, which does not combine with rubber, they have in consequence vulcanization temperatures only a few degrees below their temperatures of decomposition. In these cases vulcanizates are produced which are derived from unsubstituted rubber, whereas the halogen compounds yield vulcanizates derived from rubber which has reacted with hydrogen halide. Correspondingly the mechanical properties of the vulcanizates obtained with halogen compounds are far poorer than those obtained with phenol-dialcohols. This is evident in Tables II and IV of Part I.

Summarizing, it may be concluded that phenol-dialcohols vulcanize slowly, at temperatures only slightly below their decomposition temperatures, and yield comparatively good vulcanizates. Pseudophenol halides vulcanize rapidly at temperatures considerably below their decomposition temperatures, and yield comparatively poor vulcanizates.

DIFFERENCES BETWEEN THE VULCANIZING PROPERTIES OF 2,6-DIHYDROXYMETHYL-4-METHYLPHENOL AND 4,6-DIHYDROXYMETHYL-2-METHYLPHENOL

The important difference between the vulcanizing properties of 2,6-dihydroxymethyl-4-methylphenol and 4,6-dihydroxymethyl-2-methylphenol is manifest mainly in their temperatures of vulcanization. It is possible, for example, to vulcanize 100 parts of rubber with 40 parts of 2,6-dihydroxymethyl-4-methylphenol in 2 hours at 155° C, whereas 4,6-dihydroxymethyl-2-methylphenol requires a temperature of about 200° C for the same time.

It was shown experimentally that rubber, if vulcanized in the ordinary way in an electrical press, is attacked too strongly at that high temperature by the oxygen in the mixture. This can be improved by evacuation of the

mixture for 16 hours, vulcanization being carried out immediately afterwards. Some results of these vulcanizations are given in Table I.

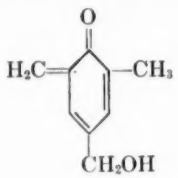
TABLE I

MECHANICAL PROPERTIES OF VULCANIZATES OF 100 PARTS OF RUBBER AND 40 PARTS OF 4,6-DIHYDROXYMETHYL-2-METHYLPHENOL

Vulcanization (minutes)	60	120	120
Vulcanization temperature (° C)	200	200	200
Tensile strength (kg. per sq. cm.)	43	36	85
Elongation at break (percentage)	480	450	490
Modulus at 100% (kg. per sq. cm.)	*	*	5
Modulus at 200%	*	*	8
Modulus at 400%	*	*	50
Hardness (Shore A)	*	*	30

* Not measured.

As is evident from these data, 4,6-dihydroxymethyl-2-methylphenol also has vulcanizing properties, although at a higher temperature. To explain this difference in regard to 2,6-dihydroxymethyl-4-methylphenol, the formation of methylene quinones in both cases must be considered. Unlike the *p*-cresol compound, the *o*-isomer is able to produce two kinds of methylene quinones, namely an *o*- and a *p*-isomer (I and II).



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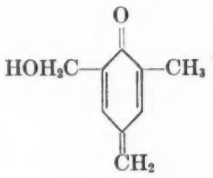
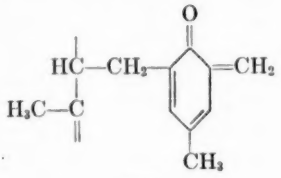


II

It may logically be assumed that the *o*-isomer (I) is the first intermediate in the process, as in general *o*-methylene quinones are formed more easily than the analogous *p*-isomers[1]. Thus, in the case of 2,6-dihydroxymethyl-4-methylphenol as well as 4,6-dihydroxymethyl-2-methylphenol, the primarily formed *o*-methylene quinone combines with a rubber chain, forming an addition compound[2]. To combine with a second rubber chain, in the first case an *o*-, in the second a *p*-methylene quinone, must be formed (III and IV).



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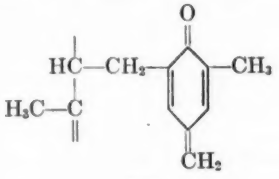


IV

As already stated, the formation of the latter compound (IV) takes place more difficultly, so a higher temperature is necessary, as was found by experiment. Finally vulcanization is completed by a spontaneous addition of the second rubber chain to these reformed methylene quinones.

The difference in vulcanization rate between 2,6-dihydroxymethyl-4-methylphenol and 4,6-dihydroxymethyl-2-methylphenol cannot be explained

by a decreased reactivity towards rubber of the *p*-methylene quinone (IV). For, in the first place, both kinds of methylene quinones have too great a reactivity to be isolated. Secondly, if the *p*-methylene quinone is formed more easily, as is the case with 4,6-dibromomethyl-2-methylphenol, the vulcanization rate is also high, comparable with that of 2,6-dibromomethyl-4-methylphenol, although differences exist similar to those with the phenol-dialcohols considered.

VULCANIZING PROPERTIES OF MIXTURES OF 2,6-DIHYDROXYMETHYL-4-METHYLPHENOL AND 4,6-DIHYDROXYMETHYL-2-METHYLPHENOL

If rubber is vulcanized in the usual way for 2 hours at 155° C with mixtures of 2,6-dihydroxymethyl-4-methylphenol and 4,6-dihydroxymethyl-2-methylphenol, the latter appears to exert a negative influence on the reaction, as is shown in Table II.

TABLE II

MECHANICAL PROPERTIES OF VULCANIZATES OF 2,6-DIHYDROXYMETHYL-4-METHYLPHENOL AND MIXTURES OF 2,6-DIHYDROXYMETHYL-4-METHYLPHENOL AND 4,6-DIHYDROXYMETHYL-2-METHYLPHENOL. VULCANIZATION TIME, 2 HOURS AT 155° C

	Mixtures					
Rubber	parts	100	100	100	100	100
2,6-Dihydroxymethyl-4-methylphenol	"	10	20	40	36	32
4,6-Dihydroxymethyl-2-methylphenol	"	—	—	—	4	8
Tensile strength (kg. per sq. cm.)		22	100	170	70	42
Elongation at break (percentage)		575	575	558	460	450
Modulus at 100% (kg. per sq. cm.)		3	6	6	5	3
Modulus at 200%		5	10	15	10	6
Modulus at 400%		8	29	83	48	29
Hardness (Shore A)		30	35	38	30	25

No vulcanization at all could be observed on using phenol-dialcohol mixtures containing 50 per cent or more of the *o*-cresol compound, 40 parts of these mixtures being employed to 100 parts of rubber in each case. In other words, no vulcanization occurred with a mixture containing 20 parts of the *o*- and 20 parts of the *p*-cresol compound. Yet it is possible to vulcanize 100 parts of rubber with only 10 parts of pure 2,6-dihydroxymethyl-4-methylphenol. From this it may be concluded that the *o*-cresol compound exerts a negative influence on the vulcanizing properties of the *p*-isomer. This behavior can easily be explained by means of the methylene quinone theory, bearing in mind first that, at 155° C, only *o*- and no *p*-methylene quinones can be formed, and, secondly, *p*-phenol-dialcohols are far more stable than the *o*-isomers[3]. From this it follows that the *o*-hydroxymethyl group of 4,6-dihydroxymethyl-2-methylphenol has a greater reactivity than the *p*-group.

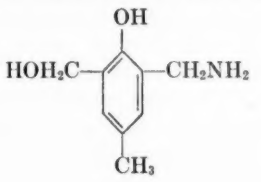
Until now the vulcanization reactions with the phenol-formaldehyde derivatives have been formulated for the sake of simplicity with only one molecule of the vulcanizing agents. But, as a matter of fact, resinification always plays a part in the process, so the bridge linkages are formed by several molecules of the phenol-dialcohols, united by means of —CH_2— or —CH_2OH_2C— bonds. Hence, if a bridge grows from one rubber chain to another in the presence of 4,6-dihydroxymethyl-2-methylphenol, that substance will preferably react by means of its *o*-hydroxymethyl group. But after that the side chain is not able

to combine with a second rubber molecule at 155° C, the formation of a *p*-methylene quinone being necessary. It is clear that, in this way, one molecule of 4,6-dihydroxymethyl-2-methylphenol is sufficient to prevent the formation of a bridge linkage by any number of 2,6-dihydroxymethyl-4-methylphenol molecules. The chance of a bridge being formed thus depends only on the number of both kinds of molecules, and is smaller if more of the *o*-compound is present. Owing to these facts, a comparatively small amount of 4,6-dihydroxymethyl-2-methylphenol has a great influence on the mechanical properties of the vulcanizates. Also the experimentally established limit of 50 per cent of the *o*-cresol compound in the mixtures, at which no vulcanization at all takes place, corresponds fairly well with these views.

INFLUENCE OF HEXAMETHYLENETETRAMINE ON THE VULCANIZING PROPERTIES OF PHENOL-FORMALDEHYDE DERIVATIVES

The influence of the well known hardening agent of the synthetic resin industry, hexamethylenetetramine, on the vulcanizing properties of phenol-formaldehyde derivatives, was studied in the case of 2,6-dihydroxymethyl-4-methylphenol. Vulcanization was carried out in the usual way, 100 parts of rubber being mixed with 40 parts of 2,6-dihydroxymethyl-4-methylphenol and 5 parts of hexamethylenetetramine, and the mixture heated at 155° C for 2 hours. No vulcanization reaction at all took place, and the mixture remained completely soluble in benzene.

This result can be explained by means of the methylene quinone theory in the following manner. In consequence of its great reactivity, the methylene quinone formed from 2,6-dihydroxymethyl-4-methylphenol reacts immediately with the ammonia liberated by the hexamethylenetetramine, with formation of a compound possessing for instance the following structure (V):



V

Compounds of this type are capable of reacting by means of their amino groups with other molecules of formaldehyde, yielding larger resin molecules, but formation of methylene quinones can take place only at one side of the molecules. And, moreover, in this latter case the methylene quinones formed react immediately with other molecules of ammonia, rather than with the large and slow rubber molecules. In this way methylene quinones are captured by the ammonia molecules before the former have an opportunity of combining with the rubber molecules. In this way the formation of bridge linkages between the rubber chains is prevented, and no vulcanization can take place.

Before the methylene quinone theory was established, the vulcanizing properties of the phenol-formaldehyde derivatives were supposed to be based on the formation of a three-dimensional net structure among the rubber molecules, rendering the whole insoluble. This supposition is not only contrary to the preceding, but could moreover be proved to be incorrect by means

of the following experiment with hexamethylenetetramine. A mixture of 1 mole of crude cresol and ⅓ mole of hexamethylenetetramine was heated at about 200° C for 30 minutes, whereby a yellow-red resin was formed. As ammonia was liberated during the reaction, the configuration of the resin must be considered to be a three-dimensional net structure, consisting of molecules of the diverse phenols linked together by CH_2-bridges.

This resin was thermosetting and initially completely soluble in benzene. Yet it had no vulcanizing properties, which is not surprising according to the foregoing. No methylene quinone could indeed be formed because of the lack of the necessary substituents. If the vulcanizing properties of the synthetic resins were based on the formation of an entangled knot of rubber and resin molecules, the resin should vulcanize rubber very well. Since, however, this is not the case, it may be concluded that such an entanglement is not equivalent to vulcanization, but that the latter is based only on the formation of primary chemical bonds.

VULCANIZING PROPERTIES OF ESTERS OF 2,6-DIHYDROXYMETHYL-4-METHYLPHENOL

The vulcanizing properties of the hydrogen halide esters of 2,6-dihydroxymethyl-4-methylphenol have already been described in the preceding sections. In this section a number of other esters are described, particularly those derived from acids of well known pseudophenol halides.

A. FATTY ACID ESTERS

The ordinary diacetate of 2,6-dihydroxymethyl-4-methylphenol, 2,6-diacetoxymethyl-4-methylphenol, could not be prepared, as it was found to decompose immediately after its formation. Even if the reactions were carried out under very mild conditions, such, for example, as shaking a mixture of 2,6-dibromomethyl-4-methylphenol and silver acetate in benzene for 18 hours at room temperature, the diacetate initially formed decomposed spontaneously with the liberation of acetic acid. Nevertheless, the influence of the acetate group could be studied with 2-chloromethyl-6-acetoxymethyl-4-chlorophenol[4] (VI). As was to be expected, this compound vulcanized rubber in a similar way to the pseudophenol halides; thus also in this case the acid group readily splits off and a methylene quinone is formed as an intermediate (see Table III).

Like the diacetate, the higher fatty acid esters could also not be prepared, as the products initially formed invariably decomposed spontaneously. No difficulties were met, on the other hand, with the preparation of the diformiate[4] (VII). Some results of vulcanizations obtained with the compounds VI and VII are given in Table III.

TABLE III

MECHANICAL PROPERTIES OF VULCANIZATES OF 100 PARTS OF RUBBER AND 40 PARTS OF COMPOUNDS VI AND VII

	VI	VII
Vulcanization time (minutes)	30	45
Vulcanization temperature (° C)	150	140
Gauge of the dumb-bells (mm.)	1	0.30
Tensile strength (kg. per sq. cm.)	14	21
Elongation at break (percentage)	165	417
Modulus at 100% (kg. per sq. cm.)	8	—
Modulus at 400%	—	20
Hardness (Shore A)	38	30

Although these mechanical properties are inferior, yet it may be concluded that the esters of phenol-dialcohols, as regards stability, possess vulcanizing properties similar to those of the pseudophenol halides; an analogous reaction mechanism must therefore be assumed.

B. RHODANIC ACID ESTER

The compound 2,6-dirhodanomethyl-4-methylphenol[4] was easily prepared, but it did not show any vulcanizing properties. This fact is very remarkable, as the compound is not only soluble in benzene but also splits off rhodanic acid very readily on heating.

The acid liberated in this particular case, however, is not stable under the conditions of vulcanization, it being a well known fact that free rhodanic acid polymerizes rapidly above 0° C. At the comparatively high temperature of vulcanization, two unstable and very reactive compounds, namely, a methylene quinone and free rhodanic acid, would be formed. It may logically be supposed that these two compounds react immediately, whereas the comparatively inactive rubber molecules are excluded from the reaction. This supposition is supported by the following experiment.

About 1 gram of the rhodanic ester was heated a few degrees above its melting point (131–133° C), and the gaseous products, liberated during the heating, passed into a 4 *N* solution of sodium hydroxide by means of a current of nitrogen. Shortly afterwards rhodanic ions were present in the solution, whereas the original rhodanic ester had formed a resin completely insoluble in benzene. Analogous experiments, carried out with 2,6-dihydroxymethyl-4-methylphenol or its halogen derivatives, yielded soluble resins. From this it follows that the insoluble resin derived from the rhodanic ester was formed by a reaction in which the unstable and reactive rhodanic acid played an important part.

From the foregoing it may be concluded that, during vulcanization, a similar resin is also produced, and no actual vulcanization can take place.

C. NITRO COMPOUNDS

Although the nitro compounds are not really esters, yet the investigations with 2,6-dinitromethyl-4-methylphenol[4] should be mentioned, as this compound behaves in a similar way to the higher fatty acid esters. This nitro compound is also unstable, and decomposes immediately and spontaneously after its formation, with the liberation of gaseous nitrogen oxide. These phenomena may be considered to be due to the liberation of nitrous acid, the reaction being analogous to the liberation of acids from the phenol-dialcoholic esters described. In consequence of that unstability, no investigation of the vulcanizing properties could be performed.

Although most of the fatty acid esters derived from 2,6-dihydroxymethyl-4-methylphenol as well as its dinitro compound are unstable, and in most cases no investigation of the vulcanizing properties could be carried out, yet these results give strong support to the supposition that methylene quinones act as intermediates in vulcanizing rubber with phenol-formaldehyde derivatives, these substances being formed with the liberation of water or acids. The above-mentioned unstable compounds show such liberation even at room temperature. Thus it may be concluded that esters which are stable at room temperature decompose at the high temperature used for vulcanizing purposes in a similar manner, splitting off acids and producing methylene quinones as intermediates.

VULCANIZING PROPERTIES OF COMPOUNDS CLOSELY RELATED TO 2,6-DIHYDROXYMETHYL-4-METHYLPHENOL

A. COMPOUNDS WITHOUT PHENOLIC HYDROXYL GROUPS

Since the phenolic hydroxyl group plays an essential part in the formation of methylene quinones, compounds without this group do not show any vulcanizing properties, no methylene quinones being formed. This was proved in the usual experimental way with the compounds 1,3-dihydroxymethyl-5-methylbenzene[6] and 1,3-dibromomethyl-5-methylbenzene[6]. The results obtained were, in accordance with the theory, completely negative.

B. COMPOUNDS WITH ALKYLATED PHENOLIC HYDROXYL GROUPS

If the phenolic hydroxyl group of 2,6-dihydroxymethyl-4-methylphenol is alkylated, as is the case, for example, with 1-methoxy-2,6-dihydroxymethyl-4-methylbenzene[7], one of the reactive substituents necessary for the formation of a methylene quinone, has been stabilized. In consequence the latter reaction cannot take place under the usual conditions of vulcanization, in other words, there will be no vulcanization. The compound proved experimentally to fulfil that expectation.

C. COMPOUNDS WITH ESTERIFIED PHENOLIC HYDROXYL GROUPS

Esterification of the phenolic hydroxyl group of 2,6-dihydroxymethyl-4-methylphenol has an influence analogous to that of alkylation. In this case also the configuration becomes more stable, and no methylene quinone can be formed under vulcanization conditions. The completely negative experimental results, obtained with the toluene sulfonic ester of 2,6-dihydroxymethyl-4-methylphenol[8] as an example, corresponded to these views.

The stabilizing influence of esterification of the phenolic hydroxyl group is particularly obvious with the pseudophenol halides, e.g., it appeared possible to determine the molecular weight of 1-acetoxy-2,6-dichloromethyl-4-methylbenzene[4] by means of Rast's method[9], it being necessary to melt the compound in camphor without decomposition.

0.0214 g. of the said compound was dissolved in 0.3460 g. of camphor. M.p. camphor: 174.7° C. M.p. mixture: 165.0° C. Lowering of the m.p.: 9.7° C.

$$\text{Mol. weight found: } \frac{40.000 \times 0.0214}{0.3460 \times 9.7} = 255.$$

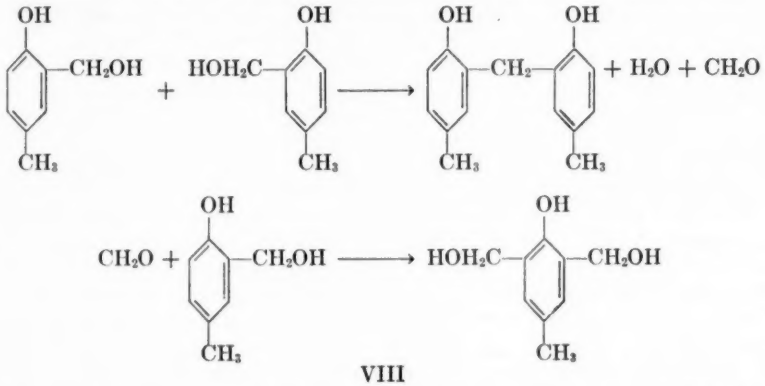
Mol. weight calculated for $C_{11}H_{12}O_2Cl_2$: 247.

From these data it may be concluded that the compound is stable even at the high temperature of 175° C. As could be expected, it did not show any vulcanizing properties.

D. PHENOL-MONOALCOHOLS

As a matter of fact, rubber cannot be vulcanized with phenol-monoalcohols according to the methylene quinone theory, for, with only one rubber chain, an addition compound can be formed. This was proved experimentally with the two compounds, 2-hydroxymethyl-4-methylphenol[10] and 2-hydroxymethyl-4-tertiobutylphenol[4]. Mixtures of 100 parts of rubber and 40 parts of these phenol-monoalcohols could not be vulcanized within 2 hours at 155° C.

Yet the latter compound still appeared to have very slight vulcanizing properties. This can easily be explained by the resinification reactions invariably taking place at the same time. These reactions generally yield a certain amount of formaldehyde liberated by the condensation between two hydroxymethyl groups. But in the case of a phenol-monoalcohol, this formaldehyde can be bound once more, at least partly, to a free reaction-favorable position of the nucleus, a molecule of phenol-dialcohol thus being formed (VIII).



VIII

Thus a phenol-monoalcohol yields a small amount of phenol-dialcohol or resol with vulcanizing properties. For that reason it was not remarkable that 2-hydroxymethyl-4-methylphenol appeared to exert a slight vulcanizing action at 200° C, yielding a vulcanizate with very bad mechanical properties. After 2 hours at 200° C in an atmosphere of nitrogen, the mechanical properties were found to be:

tensile strength, 7 kg. per sq. cm.; elongation at break, 282 per cent.

The explanation of the slight vulcanizing properties of phenol-monoalcohols is also supported by the results obtained with 2,4-dimethyl-6-hydroxymethylphenol[11]. This compound only differs from 2-hydroxymethyl-4-methylphenol by the absence of the free reaction-favorable position, this being occupied by a methyl group. In this case liberated formaldehyde cannot combine with a second molecule to form a dialcohol. For that reason no vulcanizing properties show themselves at a higher temperature, *e.g.*, 200° C; in fact vulcanization experiments carried out with this compound yielded completely negative results.

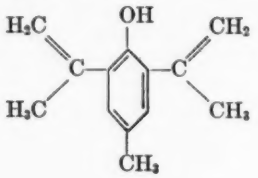
E. COMPOUNDS WITH ALKYLATED ALCOHOL GROUPS

An example of a phenol-dialcohol with alkylated alcohol groups, namely, 2,6-dimethoxymethyl-4-methylphenol[12], was already mentioned in the preceding article. The homologous compound 2,6-diethoxymethyl-4-methylphenol[4] was also prepared, and likewise had no vulcanizing properties. It seems superfluous to explain these facts in detail, as they could be expected naturally from the preceding sections: also in these cases no methylene quinones can be formed because of the great stability of the compounds.

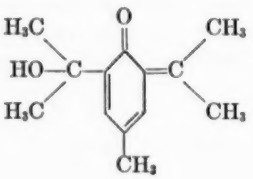
F. COMPOUNDS WITH TERTIARY ALCOHOL GROUPS

It is a well known fact that tertiary alcohols decompose easily on heating, with formation of water and unsaturated compounds. This possibility may,

therefore, also exist with 2,6-dihydroxyisopropyl-4-methylphenol[13]. On the other hand, the formation of a methylene quinone can be formulated. The products formed by these two kinds of reactions have the following configurations (IX and X):



IX



X

Which of these two possibilities is realized on heating with rubber was not investigated in detail, but it is probable that both reaction types occur. Now it is clear that Compound IX, not being a methylene quinone and not being able to pass over into that configuration, has no vulcanizing properties. Compound X on the other hand does have this configuration, but substituted, so its reactivity is much smaller than that of an unsubstituted methylene quinone. The latter fact is demonstrated also by comparing the reactivities of ordinary *p*-benzomethylene quinone and fuchsone. The first compound, an unsubstituted methylene quinone, has too great a reactivity to be isolated, whereas the latter is stable, melting at 167–168° C without decomposition. So it cannot be expected that the methylene quinone X, if indeed formed, combines readily with the rubber chains to form a vulcanizate. This was also found experimentally, the compound 2,6-dihydroxyisopropyl-4-methylphenol yielding no vulcanizate at 155° C or at 200° C.

G. COMPOUNDS WITH ALDEHYDE AND ACID GROUPS

If the two alcohol groups of a phenol-dialcohol are oxidized, a phenol-dialdehyde or a phenol-dicarboxylic acid is formed. The two compounds 2,6-dialdo-4-methylphenol[14] and 2,6-dicarboxy-4-methylphenol[15] as representatives of these classes were included in the investigation. As a matter of fact methylene quinones cannot be formed from these compounds, so vulcanizing properties were not to be expected. Experiments which were carried out to test these suppositions actually yielded negative results.

The results of the investigations described in this section may be summarized as follows. Compounds considered to be derived from phenol-dialcohols by a change in their configuration do not show vulcanizing properties if the formation of methylene quinones is out of the question. If a repeated formation of these intermediates is only possible to a very limited extent, as is the case with phenol-monoalcohols, vulcanizing properties are present to a minor degree. These observations also support the view according to which the vulcanizing properties of the phenol-formaldehyde derivatives are closely connected with the possibility of a repeated formation of methylene quinones.

SUMMARY

Referring to Part I, describing the methylene quinone theory of the vulcanization of rubber with phenol-formaldehyde derivatives, in this paper the arguments in favor of that theory are considered in detail. The results of the investigations in question can be summarized as follows.

1. The vulcanizing properties of the pseudophenol halides are based on the easy transformation of these compounds into methylene quinones, with liberation of gaseous hydrogen halide.

2. The vulcanizing properties of the phenol-dialcohols are also based on the formation of methylene quinones as intermediates, but only at higher temperatures.

3. Phenol-dialcohols vulcanize slowly at temperatures only slightly below their decomposition temperatures, and yield comparatively good vulcanizates.

Pseudophenol halides vulcanize rapidly at temperatures considerably below their decomposition temperatures, and yield comparatively poor vulcanizates.

4. The vulcanization temperature of 4,6-dihydroxymethyl-2-methylphenol (about 200° C) is higher than that of 2,6-dihydroxymethyl-4-methylphenol (about 155° C), as in the first case the vulcanization is based on the formation of an *o*-methylene quinone as well as a *p*-methylene quinone, and in the second case on the formation of *o*-methylene quinones exclusively. Generally these last compounds are formed more easily than the *p*-isomers.

5. The vulcanizing properties of 2,6-dihydroxymethyl-4-methylphenol at 155° C are reduced by the addition of 4,6-dihydroxymethyl-2-methylphenol, in consequence of the formation of molecular complexes which are unable to form *o*-, but only *p*-methylene quinones.

6. The vulcanizing properties of phenol-formaldehyde derivatives are entirely destroyed by hexamethylenetetramine, as that substance combines with the methylene quinones first formed.

7. The vulcanization reactions of the phenol-formaldehyde derivatives are not based on the formation of an irregular knot of entangled rubber and resin molecules, but on primary chemical bonds between these two.

8. The vulcanizing properties of the esters of the phenol-dialcohols, as well as those of the pseudophenol halides, are based on the formation of methylene quinones as intermediates, with liberation of acids. The higher fatty acid esters of 2,6-dihydroxymethyl-4-methylphenol are unstable, with the liberation of acids already at room temperature.

9. Compounds which may be supposed to be derived from phenol-dialcohols by a change in their configuration do not show vulcanizing properties if the formation of methylene quinones is impossible. If a repeated formation of these intermediates is only possible to a very limited extent, as is the case with phenol-monoalcohols, vulcanizing properties are also present on a minor scale.

EXPERIMENTAL PART

1. 2-CHLOROMETHYL-6-ACETOXYMETHYL-4-CHLOROPHENOL

A mixture of 66 g. of 2,6-dihydroxymethyl-4-chlorophenol and 125 cc. of glacial acetic acid was saturated with dry gaseous hydrogen chloride at room temperature. Shortly afterwards the compound crystallized and was recrystallized from a mixture of ethyl acetate and petroleum ether (boiling at 40–60° C). White crystals, melting at 101–103° C. Yield 24.4 g. = 28%.

Analysis:

Found:	C 48.14; H 4.13; Cl 28.71.
Calculated for $C_{10}H_{10}O_3Cl_2$(248.82):	C 48.20; H 4.02; Cl 28.49.

The compound decomposed on heating with dilute alkali with liberation of acetic acid.

2. 2,6-DIFORMOXYMETHYL-4-METHYLPHENOL

A solution of 1.47 g. of 2,6-dibromomethyl-4-methylphenol in 25 cc. of acetone was shaken with 1.36 g. of sodium formate for 16 hours at room temperature. After removing the precipitated sodium bromide by filtration, the acetone was distilled off under reduced pressure and the residue recrystallized from petroleum ether (boiling at 100–130° C), white crystals, melting at 75–76° C. Yield 0.51 g. = 45%.

Analysis:

Found:	C 59.27; H 5.36.
Calculated for $C_{11}H_{12}O_5$(223.92):	C 58.92; H 5.36.

3. 2,6-DIRHODANOMETHYL-4-METHYLPHENOL

To a solution of 4.9 g. of 2,6-dibromomethyl-4-methylphenol 15 cc. of acetone was added slowly a solution of 2.53 g. of ammonium thiocyanate, with constant stirring. This mixture was diluted with 15 cc. of acetone and filtered from the precipitated ammonium bromide after stirring for a short time. The acetone was removed by distillation under reduced pressure and the residue recrystallized from benzene. White crystals, melting at 131–133° C. Yield 2 g. = 48%.

Analysis:

Found:	C 52.72; H 4.04; N 11.06, 10.96.
Calculated for $C_{11}H_{10}OS_2N_2$(250.04):	C 52.76; H 4.00; N 11.20.

4. ATTEMPTED PREPARATION OF 2,6-DINITROMETHYL-4-METHYLPHENOL

A dilute solution of 2,6-dibromomethyl-4-methylphenol in acetone was shaken with three times the required amount of silver nitrite for 16 hours at room temperature. Considerable gaseous nitrogen oxide was liberated. After removing the solid by filtration and the acetone by distillation under reduced pressure, an oil was obtained which liberated gaseous nitrogen oxide continuously and could not be forced to crystallize by cooling.

The attempt was repeated, taking care by cooling that the temperature did not rise above 0° C, but exactly the same result was obtained. A viscous, orange colored oil was formed, liberating gaseous nitrogen oxide spontaneously.

From this it was concluded that the compound in question was unstable, like the acetic acid and higher fatty acid esters of 2,6-dihydroxymethyl-4-methylphenol.

5. 1-ACETOXY-2,6-DICHLOROMETHYL-4-METHYLBENZENE

To a solution of 30.75 g. of 2,6-dichloromethyl-4-methylphenol in 60 cc. of acetic anhydride was added one drop of concentrated sulfuric acid, and the mixture was shaken. Within a few minutes the compound crystallized from the solution, was filtered off, washed with water, dried, and recrystallized from petroleum ether (boiling at 80–100° C). White crystals, melting at 104–105° C. Yield nearly quantitative.

Analysis:

Found:	C 53.59; H 4.92; Cl 28.43.
Calculated for $C_{11}H_{12}O_2Cl_2$(246.82):	C 53.45; H 4.87; Cl 28.72.

6. 2-HYDROXYMETHYL-4-TERTIOBUTYLPHENOL

30 g. of 4-tertiobutylphenol were dissolved in a mixture of 40 cc. of 96% alcohol and 44 cc. of 33% formalin, after which a solution of 10 g. of sodium hydroxide in 24 cc. of water was added. After maintaining the mixture for 4 days at room temperature, the crystallized sodium salt of the phenol-monoalcohol was filtered off, washed with a solution of sodium chloride and dissolved in 1.2 l. of water. To this solution 10.5 cc. of 8 *N* sodium hydroxide was added, the solution filtered from some resinous material, and acidified with 60 cc. of 4 *N* acetic acid. The precipitated phenol-monoalcohol was filtered off, washed with water, dried, and recrystallized from petroleum ether (boiling at 100–130° C). White leaflets melting at 90–91° C. Yield 15 g. = 42%.

Analysis:

Found:	C 73.26; H 8.88.
Calculated for $C_{11}H_{16}O_2$(179.194):	C 73.32; H 8.90.

7. 2,6-DIETHOXYMETHYL-4-METHYLPHENOL

A solution of 11.76 g. of 2,6-dibromomethyl-4-methylphenol in 100 cc. of alcohol, cooled to 0° C, was mixed with a solution of 5 g. of sodium cyanide in 15 cc. of water and 10 cc. of alcohol, likewise cooled to 0° C, after which a further 25 cc. of alcohol was added. After keeping it at room temperature for 29 hours, it was boiled for ½ hour, diluted with water to 1 l., and the separated oil extracted with benzene. The extract was dried with sodium sulfate and fractionated. The compound was obtained as a colorless liquid, boiling at 120–122° C/0.50–0.55 mm. Yield 8.1 g. = 90%.

Analysis:

Found:	C 69.38; H 8.73.
Calculated for $C_{13}H_{20}O_3$(223.93):	C 69.63; H 8.94.

ACKNOWLEDGMENT

The author acknowledges his indebtedness to the Rubber Foundation for permission to publish this paper.

His thanks are also due to A. van Rossem, Director of the Research Department of the Rubber Foundation, for his great interest and constructive criticisms.

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DETERMINATION OF PEROXIDES IN SYNTHETIC RUBBERS *

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Peroxides are found in synthetic rubbers either as the result of attack by oxygen, usually from the air, or as a residue from polymerization operations employing peroxide catalysts. Because of possible detrimental effects of active oxygen on the properties of the rubber[1], a method of quantitative determination is needed.

The concentration of peroxides in substances of lower molecular weight may be determined with ferrous thiocyanate reagent, either titrimetrically as recommended by Yule and Wilson[2] or colorimetrically as by Young, Vogt, and Nieuwland[3]. Unfortunately, many highly polymeric substances are not soluble in the acetone and methanol solutions employed in these procedures. This is also the case with hydrocarbon monomers, such as butadiene, containing appreciable concentrations of soluble high molecular weight polymers[4]. Bolland, Sundralingam, Sutton and Tristram[5] recommended benzene as a solvent for natural rubber samples and the reagent made up in methanol. However, most synthetic rubbers are not readily soluble even in this combination. The following procedure employs the ferrous thiocyanate reagent in combination with a solvent capable of maintaining considerable concentrations of synthetic rubber in solution. The solvent comprises essentially 20 per cent ethanol in chloroform.

SCOPE AND ACCURACY

The procedure has been found to be applicable to Perbunan, Buna-S, Butyl, and other synthetic rubbers and plastics soluble in hydrocarbon or other solvents, or to that portion which is soluble in case the sample contains appreciable "gel". In general, it is restricted to unvulcanized samples. Highly colored samples may give difficulty in the colorimetry. The presence of fresh oxidation inhibitors, such as phenyl-β-naphthylamine, and Agerite White (*sym*-di-β-naphthyl-*p*-phenylenediamine) does not affect the results, indicating that the interaction between active oxygen and inhibitors is rather slow at ordinary temperatures. Strong oxidizing agents, of course, interfere. By this method it is possible to detect 10 parts per million of active oxygen in the polymer. Accuracy is about 5 to 10 per cent.

REAGENT

Ferrous Solution.—Dissolve 0.130 gram of potassium thiocyanate in 50 cc. of absolute ethyl alcohol, add 0.065 gram of ferrous chloride tetrahydrate, and shake the mixture until dissolved. Make 79 cc. of pure chloroform up to 100 cc. with the alcoholic ferrous thiocyanate solution, and acidify with 2 drops of concentrated sulfuric acid. The resulting reagent should become practically colorless. A precipitate of potassium chloride which usually occurs is allowed

* Reprinted from *Industrial and Engineering Chemistry, Analytical Edition*, Vol. 17, No. 7, pages 425–426, July 1945.

to settle or is centrifuged out. The reagent is stable for several hours in the dark.

PROCEDURE

Sampling.—The polymer sample should be fairly dry and as homogeneous and representative as possible. Milling in the presence of air may add peroxides. The sample need not be thoroughly dry. Dissolve about 0.60 gram, weighed to 0.01 gram, of finely cut polymer sample in 20.0 grams of benzene in a suitably stoppered vessel of such a size as to leave but little free space. Hasten solution with the aid of continuous agitation or tumbling, and if necessary, filter to remove any foreign matter. Any soluble ferric iron present in the sample undoubtedly interferes with the analysis. A correction can be made for ferric iron by following the procedure with a separate portion of the solution, omitting the ferrous salt from the above reagent.

Analysis.—By means of a pipet add one volume of polymer solution to 15 volumes of ferrous reagent. Compare the color developed with that obtained by adding 1 cc. of a standard solution instead of sample. Standard solutions may be prepared by dissolving small known weights of pure ferric chloride hexahydrate in a given volume of methanol, followed by dilution with 19 volumes of chloroform. A blank determination should also be made, employing 1 cc. of the solvent benzene instead of sample solution, and the results corrected accordingly. Comparisons are probably best made by colorimetric or spectrophotometric technique at brief periodic intervals until no further change is observed. A Diller photoelectric colorimeter was employed in the present work. The optimum spectral distribution for absorption by ferric thiocyanate solution has already been demonstrated[6]. It may be necessary to dilute the sample solution in benzene with an additional known weight of the same solvent to make the observation in a favorable range of optical density. This range was attained with 0 to 25 p.p.m. of active oxygen in the polymer solution.

TEST OF THE METHOD

The time required for various peroxides to give maximum color density with the reagent varies considerably. Table I indicates some relative rates

TABLE I

TIME FOR MAXIMUM COLOR DENSITY

Peroxide	Time for complete reaction (min.)
Benzoyl	75
Ascaridole	60
tert-Butyl hydroperoxide	5
Butyl rubber, air-peroxidized	10
Perbunan, air-peroxidized	10
Buna-S, air-peroxidized	10
Isoprene, air-peroxidized	5
Dimer of butadiene, air-peroxidized	20

at room temperature and with an initial concentration of 10 p.p.m. of active oxygen in the sample solution.

It is evident that the hydroperoxides react the more rapidly and that the peroxides in the rubber are indicated to be largely of this type. These observations are in agreement with those of Farmer and Sutton on polyisoprene[7]. The response of the ferrous reagent to benzoyl peroxide may be accelerated by gentle warming of the test mixture.

Bolland, Sundralingam, Sutton and Tristram[5] have pointed out the severe difficulties involved in preparing polymeric mixtures containing known concentrations of peroxide by direct reaction of oxygen. As an approximation thereto, however, known mixtures were prepared for the present investigation with commercial peroxides in benzene solution and analyzed in the absence and and presence of Buna-S (Table II). Values obtained in the presence of the

TABLE II

ANALYSIS OF KNOWN MIXTURES

Peroxide used	Rubber added	Active oxygen in solution: Synthesis (*p.p.m.*)	Active oxygen in solution: Found (*p.p.m.*)
Benzoyl	None	2.5	2.3
		5.0	5.5
		9.6	10.0
		9.8	10.2
		14.7	15.0
		15.5	15.8
		18.7	18.7
		26.7	26.7
	Buna-S	10	12
		20	23
tert-Butyl hydroperoxide	None	4.8	4.1
		11.2	11.3

rubber were corrected for the small original active oxygen content of the rubber as determined in a separate analysis.

Since many synthetic rubbers contain stabilizers (antioxidants) of some kind, attempts were made to learn whether such compounds have any effect on the determination. Phenyl-β-naphthylamine and Agerite White equivalent to 0.05 and 0.20 weight per cent, respectively, based on the polymer solution, were added to Butyl and to Buna-S dissolved in benzene. Peroxide determinations resulted as follows.

Polymer	Active oxygen found inhibitor absent: P.B.N. (*p.p.m.*)	Active oxygen found inhibitor absent: A.W. (*p.p.m.*)	Active oxygen found in presence of inhibitor: P.B.N. (*p.p.m.*)	Active oxygen found in presence of inhibitor: A.W. (*p.p.m.*)
Butyl	142	25	138	24
Buna-S	45	15	47	15

It can be concluded that these inhibitors do not affect the analysis.

ACKNOWLEDGMENTS

The authors thank those among their colleagues who aided with the work and the manuscript, particularly John Rehner for helpful consultation, and the Standard Oil Development Co. for permission to publish this work.

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COMPARISON OF PLASTICITY VALUES AS DETERMINED BY THE WILLIAMS PARALLEL-PLATE AND MOONEY PLASTOMETERS

PART I*

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SUMMARY

A preliminary comparison of plasticity readings by the Mooney and Williams parallel-plate plastometers shows that, for stocks of similar type, the two readings are closely related, but the relationship is different for different types of stocks, being dependent on the value of the exponent n in the plastic flow equation.

INTRODUCTION

The adoption of the Mooney shearing-disc plastometer as the standard instrument in the United States for measuring the plasticity of raw and milled GR-S (Specification for GR-S, Rubber Reserve Company, Washington, October 1, 1943) has resulted in the question being raised as to the relation between plasticity readings obtained by this instrument and the parallel-plate plastometer.

The parallel-plate plastometer is probably the commonest instrument for measuring plasticities in this country, and, owing to the war-time difficulty of obtaining new instruments such as the Mooney plastometer, it would be an advantage to construct a table for converting the values from one instrument to those of the other.

EXPERIMENTAL

Eleven different stocks were prepared, of the types given in the table, and the plasticities were determined as follows:

(*a*) Parallel-plate plastometer. 1-cc. cylindrical pellets about 1.1 cm. high were compressed at 100° C, under a load of 5 kg., and thickness readings were taken at intervals up to 30 minutes.

(*b*) Mooney shearing-disc plastometer (large rotor) at 100° C. Two determinations on each stock were made, the plastometer being run until a constant reading was obtained, usually 4–6 minutes.

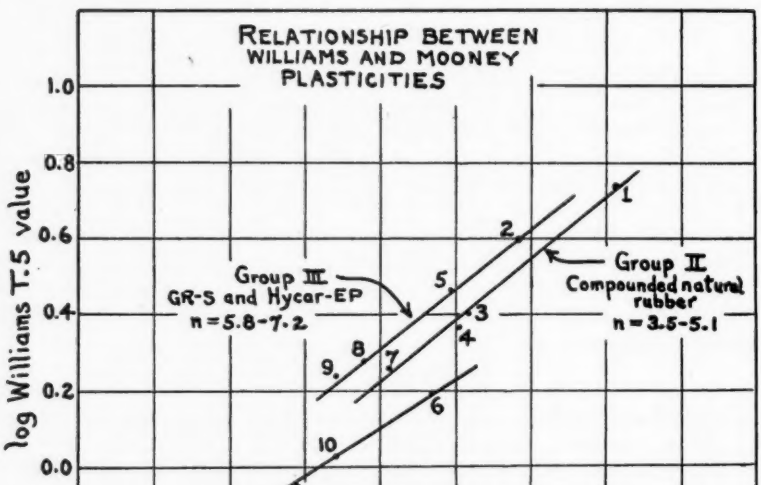
The stocks showed little change in plasticity with time. Dates of milling and plasticity measurements were as follows. All the compounds except Nos. 4 and 8 were mixed on October 19, 1943, and stock 8 on February 8, 1944, while stock 4 was a prewar tire tread. Parallel-plate measurements were carried out on November 1–12, 1943, and Mooney plastometer measurements on November 7–29, 1943, which were kindly determined by the staff of the British Rubber Producers' Research Association.

* This is Report No. 216, dated March 28, 1944, of the Research Association of British Rubber Manufacturers.

RESULTS

Results are shown in the table, in which T. 1, T. 5 and T. 30 are the thickness (mm.) after 1, 5 or 30 minutes' compression in the parallel-plate plastometer; the T. 5 values are plotted against the Mooney values in the diagram, using logarithmic scales. The values of n are derived from the equation: rate of shear = $(f/v)n$, where f is the shear stress, v is a viscosity constant, and n is a numerical constant.

Mix No.	Composition	Mooney value	T. 1	T. 5	T. 30	n
1	Natural-rubber carbon-black masterbatch	168.5	6.23	5.49	4.82	4.2
2	GR-S carbon black masterbatch	94.5	4.27	3.95	3.60	7.2
3	Reclaim natural rubber tire-tread	66.5	2.83	2.45	2.22	5.1
4	Natural-rubber tire-tread	65.0	2.65	2.28	2.01	4.8
5	GR-S tire-tread	61.5	3.07	2.82	2.51	5.8
6	Natural-rubber masticated 15 minutes	54.0	2.02	1.52	1.09	1.6
7	GR-S after thermal treatment	40.5	2.14	1.80	1.42	3.5
8	Hycar-EP tire-tread	35.5	2.07	1.84	1.71	6.7
9	GR-S masticated 15 minutes	30.0	2.10	1.73	1.28	—
10	Natural-rubber masticated 30 minutes	30.0	1.43	1.03	0.69	1.2
11	Natural-rubber masticated 60 minutes	8.5	0.73	0.49	0.31	1.1



The following conclusions are drawn.

(1) The Mooney plasticity values place the stocks roughly in the same order as do the parallel-plate plasticities (*e.g.*, T. 5 values); the more plastic the stock, the lower the Mooney value. The chief exceptions are No. 6 and No. 10 (rubber masticated 15 and 30 minutes).

(2) In the case of stocks of widely differing composition, there is no simple relation between the Mooney and the parallel-plate plasticities.

(3) The diagram shows that the results for each type of stock lie on a straight line, suggesting that, within any given type of stock, Mooney values can be converted to parallel-plate plasticity values by reference to a graph, such as that shown in the diagram. The T. 1 values give graphs very similar to those in the diagram, except that the line for uncompounded natural rubber lies a little nearer to the others.

Conclusion (2) is in accordance with expectation, since the two methods measure plasticities at widely different rates of plastic flow. The mean rate of shear in the Mooney plastometer is 0.8 per second, while the rate of shear in the parallel-plate plastometer ranges from zero up to about 0.07 per second, depending on the thickness of the pellet. This has been discussed in Report R. 203, which compares the hot and cold plasticizing of GR-S in the Banbury; hot masticated GR-S was softer than the cold plastometer (high rate of shear), while measurements by the parallel-plate plastometer (low rate of shear) indicated the reverse.

The relation between shearing stress and plastic flow of rubber stocks is not a simple one, and, as the stress is increased, the rate of flow increases far more rapidly in some cases than others. Thus the plasticity property of a stock cannot in general be characterized fully by a single constant to be known as the "plasticity value" of the stock, but requires at least the two constants v and n. This may be the reason why some manufacturers have not found simple relationships between plasticity measurements with the Mooney, extrusion, or parallel-plate plastometers in testing GR-S (see Report No. 43, Rubber Control Circular No. S. 5). It thus appears desirable to measure the shearing stress at several definite rates of plastic flow.

Conclusion 3 is in accordance with theory, which indicates that the relation between Mooney and parallel-plate readings depends on the value of n; thus the stocks in Group I (see Diagram) have n values of 1.1–1.6; those in Group II, 3.5–5.1; and those in Group III, 5.8–7.2.

PART II *

SUMMARY

Following up a previous conclusion (Reports No. 205 and 216) that the lack of a close relationship between plasticity figures obtained by the Mooney and parallel-plate instruments is due to the former giving a much higher rate of shear, it is now found that parallel-plate values obtained under conditions that give high shear-rates agree much better with Mooney values than do those obtained under the usual (low rate of shear) conditions. In the parallel-plate test a high rate of shear can be obtained by taking readings after a short compression period, by increasing the compressive force, or by reducing the volume of the specimen. These results thus suggest that the parallel-plate test, operated under appropriate conditions, might be made a satisfactory alternative to the Mooney test.

INTRODUCTION

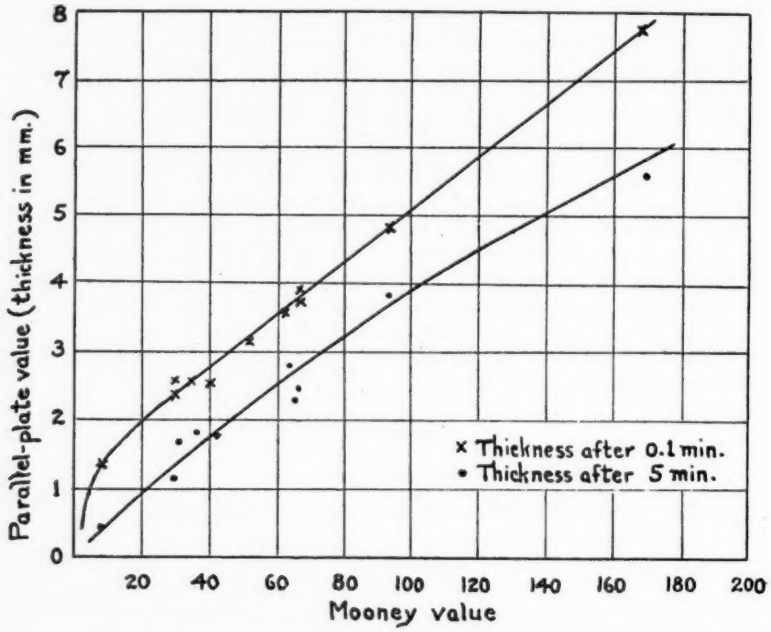
In Part I it was shown that, among a varied selection of natural rubber and GR-S stocks, the results obtained with the Mooney and parallel-plate plas-

* This is Report No. 243, dated August 24, 1944, of the Research Association of British Rubber Manufacturers.

tometers were not closely related. Similar evidence was afforded by results in an earlier report (R205), where the two forms of test indicated opposite conclusions as to the relative plasticities obtained by different mastication methods. These discrepancies were ascribed to the fact that the Mooney test produces a much higher rate of shear than the parallel-plate test. It seemed desirable, therefore, to determine whether data for a high rate of shear could be deduced from parallel-plate results and, if so, whether these would show closer agreement with Mooney values.

COMPARISON OF HIGH SHEAR-RATE DATA FROM PARALLEL-PLATE PLASTOMETER WITH MOONEY VALUES

In the parallel-plate test the mean rate of shear ("mean" because at any instant the rate varies from one part of the specimen to another) decreases as the time of compression increases (see later). Consequently if the time/thickness curve can be extrapolated back to very short times, thickness values



corresponding to high shear-rates can be obtained. This procedure has been applied to the parallel-plate data in Part I, using a logarithmic time scale, and plotting either thickness, log thickness, or log/log thickness, according to which gave most nearly a straight line.

It was thus found that, as compression time was shortened, the relation between thickness and Mooney value became closer, and was closest at about 0.1 minute. The relevant data are plotted as crosses in the graph, which shows that the relationship is much closer than when the 5-minute parallel-plate readings were used (shown by dots).

Applying the same procedure to the 60-minute masticated samples of the earlier report (R205) gave the following values: cold mastication 2.69; hot

mastication 2.52; as the corresponding Mooney values were 35 and 25, the parallel-plate and Mooney tests now agree in showing cold mastication to give the higher value.

The results thus confirm the theoretical expectation that parallel-plate results obtained at a high rate of shear agree better with Mooney values. It thus appears that, by appropriate choice of test conditions, the parallel-plate instrument may give results sufficiently nearly related to Mooney values to be usable in place of them. The theoretical basis of an approach to this problem is outlined below.

MEAN SHEAR RATE IN THE PARALLEL-PLATE PLASTOMETER

If it is assumed, as a convenient approximation, that in rubber stocks the rate of shear is proportional to (shear stress)^n, where n is a numerical constant, it can be shown that the effective mean rate of shear in a specimen compressed between parallel plates is $KDV^{\frac{1}{2}}T^{-5/2}$, where V is the volume of the specimen (cc.), T is its thickness (cm.), D is the rate of decrease in thickness (cm. per sec.), and K is a constant which depends on n and ranges from about 0.4 to 0.8.

For a given rubber stock, it can be further shown that the mean rate of shear is proportional to $(P^3/V^2t^5)^{n/(5n+3)}$, where P is the compressive force and t the time of compression. It follows that rate of shear can be increased by increasing P, reducing V, or reducing t, this last being theoretically the most effective. To what extent these means prove feasible and successful in practice is a matter for further investigation.

COMPRESSION-TEAR TEST FOR SUSCEPTIBILITY TO ROAD-CRACKING OF SYNTHETICS *

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One of the outstanding weaknesses of GR-S rubber in tire-tread formulations is a pronounced tendency to crack in road service. In general cracks originate at the bottom of cuts or of moulded grooves in the tread, but spontaneous cracking may originate from local weak spots in the interior of the tread. Properly formulated natural rubber stocks are not susceptible to this type of failure, and usual laboratory and plant criteria and test methods developed by long experience for natural rubber formulations have been proved inadequate and misleading with respect to the evaluation of the susceptibility of GR-S rubber to this type of failure.

These considerations have led to the development of the compression-tear test for susceptibility to cut growth which is the subject of this paper. The underlying principle of the test is to develop, under static easily controlled laboratory conditions, the type of strain which is the normal resultant of impact shocks of indeterminate severity under road service conditions. When pressure is applied at the surface of a cut or groove in a tire tread, the usual result is to pinch the walls of the cut together at the surface and to force them apart midway of the cut, thus producing a shearing force on the rubber under compression at the bottom of the cut. The U. G. I. compression-tear test is designed to set up a shearing force under conditions of high compression at elevated temperatures at the bottom of a standardized cut, and to measure the rate of cut growth with time.

It was suggested that this type of test be applied to a graded series of typical tire formulations. We have been advised that the compression-tear data have been successful in rating these formulations in the order of crack resistance as indicated by their road history. Complete physical measurements of these same formulations show that this is not true of any other of the standard laboratory tests. It may be noted as further confirmation that a natural rubber tread composition gave zero cut growth on compression-tear test; also that a synthetic formulation in which 35 per cent of the GR-S rubber is replaced by natural rubber gives compression-tear results most closely approaching 100 per cent natural rubber. These findings are in complete agreement with all road testing experience.

In general, when any related series of synthetic rubber formulations are arranged in the sequence of their compression-tear resistance, such increase is accompanied by unrelated changes in other desirable properties, as tensile strength, elongation and hysteresis. Hence the optimum balance for various softeners remains to be worked out by further road tests of properly selected experimental formulations. It is of particular interest that the Winkelmann

* Reprinted from the *India Rubber World*, Vol. 3, No. 1, pages 63–64, 112, October 1944.

tear values do not show the same order as the compression-tears in the case of the 100 per cent synthetics, although this test does serve to distinguish broadly between natural rubbers on the one hand and synthetics on the other.

The fact that maximum compression-tear resistance involves compromises with respect to other desirable physical properties of synthetic rubbers, such as tensile strength, elongation and hysteresis, shows the importance of a reliable laboratory technique for determining the relative susceptibility of experimental formulations to road cracking. Verification of these observations on a larger scale should greatly accelerate the improvement of GR-S tire-tread formulations.

DESCRIPTION OF COMPRESSION-TEAR TEST METHOD

A press is required which is capable of maintaining a 2,000 p.s.i. load on the sample and whose plates are thermostatically regulated to 135° ± 5° C. At the U.G.I. Laboratory, a Carver laboratory hydraulic press is used (see

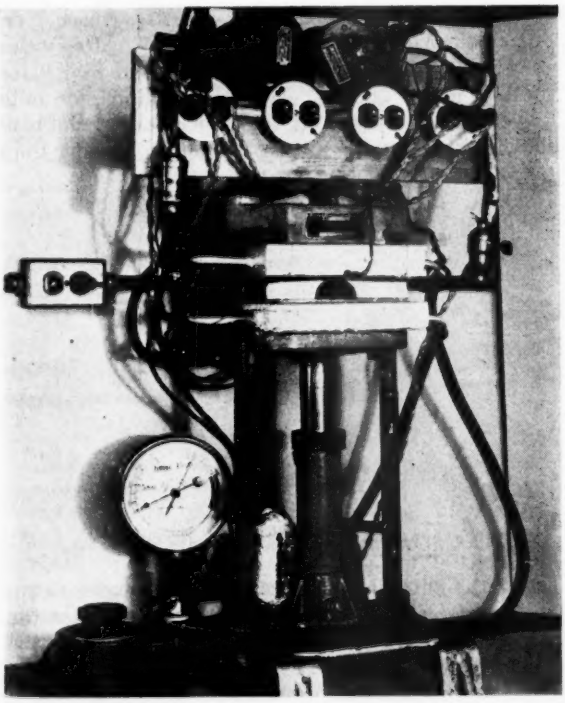

FIG. 1.—Carver laboratory press and equipment for compression-tear test.

Figure 1), having four heating units placed in each platen. The two outer units in each platen are heated continuously from a 50-volt circuit controlled by a Variac. The two inner heaters in each platen are controlled individually through a relay operated by a thermostat in the platen. The pressure is set by the gauge.

PREPARATION OF TEST SAMPLES

Test samples must be specially prepared. The unvulcanized stock to be tested is "refined" on a laboratory mill in the customary manner, and is then sheeted out in a layer ¼-inch thick. Disks approximately two inches in diameter are cut from the ¼-inch sheet and piled on top of one another to the height of the mould (about one inch), and the pile of disks is then cut in half, ready for filling the moulds. Between 65 and 70 grams of material are required for each pair of half cylinders, which must be enough to insure firm bonding of the individual disks without visible lamination after vulcanization. Should lamination cracks appear at the circumference of the test-piece, indicating poor bonding in vulcanization, it should be discarded without testing. If an extrusion machine of proper orifice is available, this difficulty in preparation of samples is avoided.

The mould provides a number of semicylindrical cavities, two inches in diameter and one inch thick. It is made by drilling two-inch holes in a steel plate one inch thick. These holes are then bisected by steel plates to form semicylindrical cavities.

Three cures are made at 115, 143 and 215 minutes, respectively, at 280° C, or the equivalent cures made for each stock tested. After vulcanization, the semicylinders of rubber are removed from the mould and placed in a mitre box to make the test cut. This is between eight and nine millimeters deep. One view of the vertical cut is seen at the upper part of the test-piece in Figure 2. The following precautions must be taken in making the cuts: (1) care

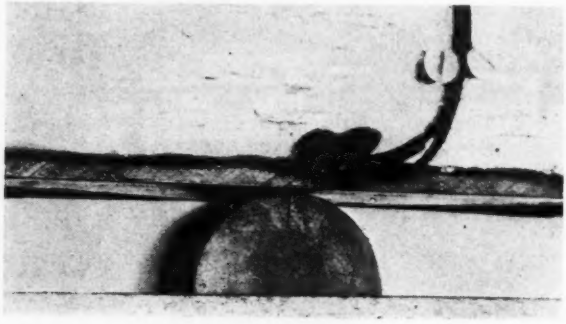

FIG. 2.—Uncompressed test-piece showing vertical cut.

must be taken that the cut is straight and at right angles to the surface, and to the edge of the cylinder; (2) care must also be taken that the depth of the cut is within the prescribed limits. Too deep a cut tends to grow more rapidly under pressure and gives poor checks. Too shallow a cut may not open properly in the center (see Figure 3) when the pressure is applied. Cuts that do not open will not grow at the normal rates, and therefore will not give comparable results.

TESTING PROCEDURE

The test-piece is placed in the press between the heated platens, as shown in Figure 1, and allowed to stand one minute at zero gauge pressure to get up to temperature. A gauge pressure of 2,000 p.s.i. is then applied for 10 minutes. After compression, the face of the test-piece should be observed by the operator

to make certain the cut has opened properly. The pressure is then released; the test-piece is removed, and the length of the cracks, or cut growth, on each side of the test-piece is measured in millimeters. The compression-tear value is the sum of the cracks, including any branches, divided by two, *i.e.*, the average cut growth per side.

"Spontaneous cracks", that is, cracks, if any, which do not originate from the original cut, are also measured and recorded separately. Such cracking is of relatively irregular incidence, but is not without significance, if a sufficient number of observations are averaged.

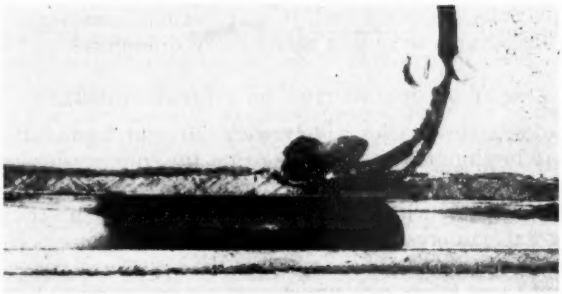

FIG. 3.—Test-piece compressed showing proper opening of cut.

The above procedures are repeated twice more, giving a total of 30 minutes' compression unless the growth in the first or second period reaches the limiting boundaries of the test-piece. No test is continued if the average growth exceeds 10 millimeters per side in the first or second 10-minute intervals, since road tests indicate that such stocks are too poor to be of further interest. The final measurements after the third 10-minute period give the accepted compression-tear value for a given test-piece, unless the test is terminated earlier as noted above. Duplicate determinations (two half-cylinder test-pieces) are made on each of three cures. Therefore the final compression-tear value represents an average of six individual test-pieces.

DEVELOPMENT OF THE NEW METHOD

As stated above, the factors in the apparatus which directly affect the extent of cracking or "cut growth" are, respectively, pressure, temperature, and time. To make the tests in the shortest possible time, the highest practicable pressure and temperature have been selected. The limits are set by the necessity of avoiding excessive permanent deformation in the test-pieces. For the usual range of hardness a gauge pressure of 2,000 p.s.i. will compress the height of the test-piece between apex and base by about 60 per cent (see Figures 2 and 3). If the compression is too great, it not only causes excessive permanent deformation, but alters the character of the resultant strains set up at the bottom of the cut. On the other hand, lower compressions unduly extend the time required to develop measurable cut growth.

A temperature of 135° C was adopted for two reasons: first, because this is not far from the temperatures which may be actually reached under heavy service conditions; and second, because higher temperatures are also found to result in excessive permanent distortion of the test-piece, and less reproducible cut growth.

With the temperature and pressure constants of the test established by the considerations above, the time or duration of pressure becomes the control variable for adjusting the severity of the test to the resistance of the test-piece. In weak specimens the cracks may approach the boundaries of the test-piece in 10 minutes. On the other hand more resistant specimens require 30 minutes to develop any measurable cracking. The intermittent application of pressure for very short time intervals was found to give results not measurably different from a continuous pressure for the same total length of time. Hence the routine finally adopted is to use consecutive pressure periods of 10 minutes each and to measure the cut growth after each such period. If much more resistant formulations are developed, it may become necessary to extend the test period to 60 minutes to obtain satisfactory differences.

EFFECT OF CURING TIME ON COMPRESSION-TEAR

The effect of overcure varies widely with different formulations. Experience to date may be summed up by saying that the compression-tear resistance of the poorer stocks appears to be extremely sensitive to extent of cure: the resistance falls off rapidly with overcure. On the other hand the better stocks show relatively flat compression-tear curves *vs.* time of cure. Road case histories are not yet sufficient to show whether the best correlations are obtained by an average of three cures, *viz.*, undercure, normal cure, and overcure, as at present, or by one of these alone. It appears probable that, ultimately, the undercure at least may be dropped from the averages with corresponding simplification of the test.

EFFECT ON COMPRESSION-TEAR OF HEAT AGING THE TEST PIECES

Very poor stocks are easily identified without heat aging. The compression-tear values of the more highly resistant stocks do not seem to be substantially affected by aging test-pieces for 24 hours at 100° C. If anything, there is some improvement. Hence no additional information of value seems to be gained by this added complication. Such a result is quite consistent with the compression-tear curves at overcure levels.

COMPRESSION-TEAR AT CONSTANT DEFLECTION VS. CONSTANT LOAD

A natural question is whether the compression-tear determinations would be better made at constant load or at constant deflection. When using equipment like the Carver press, equipped with pressure gauge, constant-pressure readings are much simpler to make than exact linear measurements of the amount of compression. However preliminary experiments were made, respectively, at 2,000 p.s.i. gauge pressure and at a constant compression of 60 per cent of the height of the test-piece. These data showed no appreciable differences between the two methods in the compression-tear values as long as the Shore hardness of the test-pieces differs by less than five points. On the other hand if hardness differences are greater than five points, the harder stocks show relatively greater compression-tear at constant compression than at constant load. Present road history is not sufficient to show which procedure gives the better road correlations over a wide range of hardness.

DETERMINATION OF UNSATURATION IN BUTYL RUBBER *

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In a recent publication[1] on unsaturation in Butyl rubber it was pointed out that, of the various methods that had been examined, ozone degradation at the double bonds appears to give the most reliable unsaturation data, the values based on the limiting viscosity of the degraded polymer being in reasonably good agreement with those determined by end-group analyses. This paper describes in some detail the analytical method, together with certain modifications that have been introduced with the aim of facilitating routine work.

It was recognized that the earlier procedure had the disadvantage of being too time-consuming, owing mainly to the steps in which the degraded polymer solution is evaporated to dryness, and the residue redissolved in diisobutylene before the viscosity measurement. An obvious possible improvement was to develop a procedure whereby the polymer solution could be ozonized and the viscosity of the degraded solution determined directly, thus eliminating evaporation and transfer to a second solvent. It was first necessary, however, to perform the experiments described below; their significance will be explained in the sequel. A further simplification was introduced through the use of carbon tetrachloride of ordinary reagent grade instead of the highly purified solvent. While this substitution usually leads to viscosity-time curves displaying a small negative slope in the region where the purified solvent gives unchanged viscosity values, a simple extrapolation to zero time gives viscosity data that are satisfactory within the limits inherent in the method. In view of the practical requirements of the method and the magnitude of the experimental error, the extra time and effort involved in further purification of the solvent appear to be unwarranted.

DEPENDENCE OF VISCOSITY IN CARBON TETRACHLORIDE ON CONCENTRATION AND MOLECULAR WEIGHT

As it is always necessary to determine the intrinsic viscosity from data obtained at finite polymer concentrations, experiments were carried out to find the effect of concentration and molecular weight on the viscosity. The intrinsic viscosity $[\eta]$ is defined by the relation:

$$[\eta] = (2.303 \log \eta_r/c)_{c\to 0} \qquad (1)$$

where η_r is the viscosity of the solution relative to that of the solvent, and c is the solute concentration expressed in grams per 100 cc. of solution. It is evident that if the function given in Equation 1 varies strongly with concentration, an appreciable error might be introduced in determining $[\eta]$ from a single measurement.

* Reprinted from *Industrial and Engineering Chemistry, Analytical Edition*, Vol. 17, No. 6, pages 367–370, June 1945.

Polyisobutylene samples covering a wide range of molecular weights were dissolved in carbon tetrachloride at various concentrations, and the viscosities of the solutions were measured at 20° C. (It is known[2] that the viscosity-molecular weight relationship for polyisobutylene is virtually identical with that for Butyl rubber.) The results are plotted in Figure 1. For polyisobutylenes of higher molecular weights the curves have a negative slope which increases with increasing molecular weight. For polymers of sufficiently low molecular weight, such as are obtained on ozonolysis of Butyl solutions, the slope is observed to be practically zero. With such polymer species it is, therefore, possible to use Equation 1 directly without imposing the limiting condition. This is a fortunate advantage, since the precision of the viscosity measurements increases considerably with increasing polymer concentration. The practical aspect of the behavior becomes more evident on inspecting the data given in Table I. It is seen that almost any Butyl rubber ordinarily encountered gives, on ozonolysis, a degraded product, the viscosity function

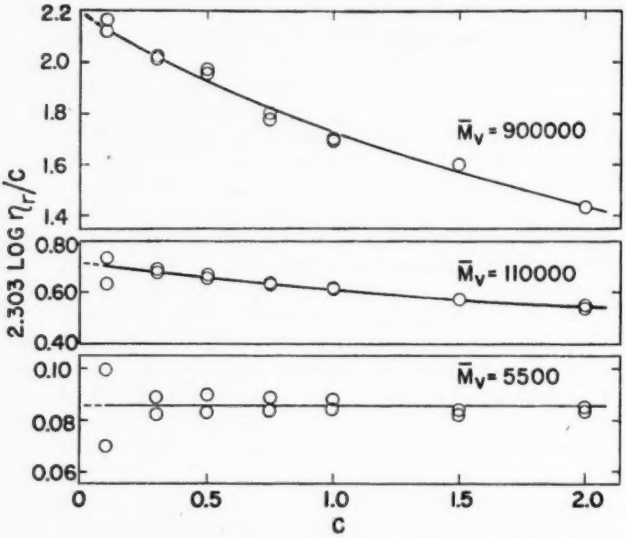

FIG. 1.—Effects of concentration and molecular weight on viscosity function in carbon tetrachloride.

TABLE I

CALCULATED MOLECULAR WEIGHT DATA FOR BUTYL RUBBER DEGRADED BY OZONE

Unsaturation of original rubber	Ozonized polymer	
	Number-average molecular weight	Viscosity-average molecular weight
Mole-per cent	$\bar{M}_n$	$\bar{M}_v$
0.1	56,100	102,800
0.5	11,200	20,560
1.0	5,610	10,280
2.0	2,805	5,140
3.0	1,870	3,425
4.0	1,403	2,570

of which is practically independent of polymer concentration in carbon tetrachloride, within the limits shown in Figure 1. GR-I, for example, has an unsaturation value of approximately 1.0 mole-per cent, and the degraded material has a viscosity-average molecular weight of roughly 10,000.

CORRESPONDING VISCOSITIES OF BUTYL RUBBER IN CARBON TETRACHLORIDE AND DIISOBUTYLENE

In general, the intrinsic viscosity of a polymer depends on the nature of the solvent. To determine the molecular weight and subsequently the original unsaturation from the intrinsic viscosity of the degraded material in carbon tetrachloride, the corresponding intrinsic viscosity in diisobutylene must be known, since it is only with the latter solvent that the relationship of viscosity

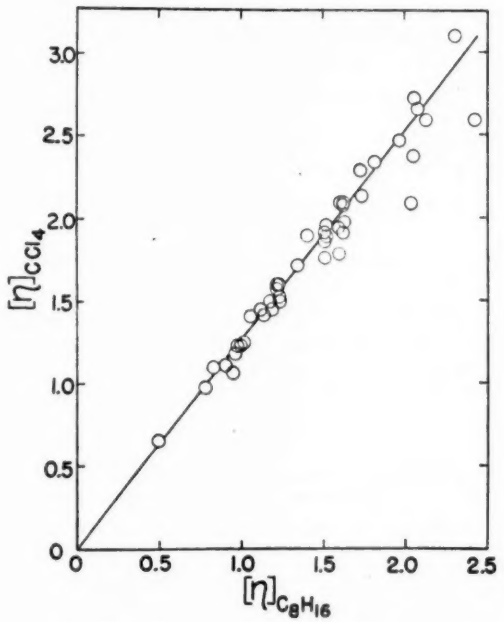

FIG. 2.—Corresponding values of intrinsic viscosity in carbon tetrachloride and in diisobutylene.

to molecular weight has been previously determined[3]. Corresponding viscosities at 20° in the two solvents were therefore measured for a series of nine Butyl rubbers. The unsaturation values of these samples ranged from 0.6 to 1.7 mole-per cent. Five of the samples were each fractionated into from 6 to 9 fractions; the remaining samples were milled with and without addition of small percentages of zinc stearate and phenyl-β-naphthylamine. A plot of the results is given in Figure 2. It is seen that the intrinsic viscosities in the two solvents are directly proportional, within the limits of error. From the original data it was found that:

$$K = [\eta]_{CCl_4}/[\eta]_{\text{Diisobutylene}} = 1.255 \pm 0.005 \qquad (2)$$

The straight line in Figure 2 is obtained from Equation 2.

STABILITY OF OZONIZED BUTYL SOLUTION

It was important to determine whether secondary changes occur when the ozonized solution (which may contain some dissolved ozone) is allowed to stand for any appreciable time, for the analyst may not find it expedient to determine the viscosity until, say, the following day. A solution of a Butyl rubber containing no added antioxidant was prepared in carbon tetrachloride, and ozonized for 4 hours. The ozonized oxygen stream was then discontinued, and dry air was passed through the solution to sweep out dissolved ozone. Aliquot samples of the solution were removed at known intervals and were allowed to stand in glass-stoppered containers until the following day. The polymers were then recovered by evaporation and their unsaturation values determined from the respective viscosities in diisobutylene. The experiment was repeated with a second sample of the same polymer. The average unsaturation values are given in Table II. It is seen that, within the experimental

TABLE II

EFFECTS OF AERATION AND AGING ON STABILITY OF OZONIZED BUTYL SOLUTION

Aeration time, minutes	0	30	60
Average unsaturation, mole per cent	1.4_0	1.4_0	1.3_2

(Unsaturation for unaged solution, 1.4_1)

error, no significant viscosity change occurs when the solution is allowed to stand overnight, and aeration after ozonization appears to be an unnecessary precaution. It is of interest, however, that even after one hour of aeration, a positive test for ozone could be obtained for the solution (by the potassium iodide test), although no odor of ozone was detected. This result may be due to the development of peroxides or to decomposition products of the solvent.

TABLE III

EFFECTS OF MILLING AND ADDITION AGENTS ON UNSATURATION VALUES OF BUTYL POLYMERS

Polymer and treatment	Intrinsic viscosity in carbon tetrachloride, by extrapolation	Corresponding intrinsic viscosity in diisobutylene	Unsaturation, (mole per cent)	Average unsaturation and probable error of single observation
I (*a*)	0.20_3	0.16_2	0.7	
(*b*)	0.24_0	0.19_1	0.5	
(*c*)	0.19_7	0.15_7	0.7	0.6 ± 0.06
(*d*)	0.23_7	0.18_9	0.5	
(*e*)	0.22_0	0.17_5	0.6	
II (*a*)	0.16_0	0.12_7	1.0	
(*b*)	0.15_8	0.12_6	1.0	
(*c*)	0.14_1	0.11_2	1.2 (?)	1.0 ± 0.03
(*d*)	0.15_6	0.12_4	1.0	
(*e*)	0.14_9	0.11_9	1.1	
III (*a*)	0.14_3	0.11_4	1.2	
(*b*)	0.15_4	0.12_3	1.1	
(*c*)	0.12_7	0.10_1	1.4	1.3 ± 0.10
(*d*)	0.13_4	0.10_7	1.3	
(*e*)	0.13_8	0.10	1.3	

EFFECTS OF MILLING AND ADDITION AGENTS ON UNSATURATION VALUES

Experiments were carried out to determine whether the presence of zinc stearate and phenyl-β-naphthylamine affects the analytical procedure. Polymers of varying degrees of unsaturation were synthesized in the absence of these substances and were treated in the following ways:

(*a*) Original polymer
(*b*) Milled for 5 minutes at 150° F, with 0.05-cm. (0.02-inch) mill roll setting
(*c*) Milled as in (*b*), with 2.5 parts of zinc stearate
(*d*) Milled as in (*b*), with 0.5 part of phenyl-β-naphthylamine
(*e*) Milled as in (*b*), with 2.5 parts of zinc stearate and 0.5 part of phenyl-β-naphthylamine

The unsaturation values were determined and are given in Table III. Within the limits of error, which is of the order of 0.1 mole-per cent, the addition agents and the milling treatment show no significant influence on the determined values.

APPARATUS AND PROCEDURE

The ozone generator is of the familiar Siemens type and is operated at 15 kilovolts.

To obtain higher ozone concentrations, oxygen is used in preference to air. Commercial oxygen is taken from a cylinder through a reduction valve and is passed, in turn, through 30 per cent sodium hydroxide, Drierite, a flowmeter, and into the generator. The ozonized gas passes from the generator through 30 per cent sulfuric acid, anhydrous calcium chloride, and into a glass manifold. A flow rate of 10 to 15 cc. per second is commonly used; this may be varied considerably and is not critical. The ozone concentration depends on the flow rate, as well as on the particular generator. At the above flow rate the apparatus used in this laboratory gives ozone concentrations of 0.14 to 0.18 per cent with air, and 0.39 to 0.56 volume per cent with oxygen. It was found that at least within these limits, the ozone concentration is not important.

The various glass leads between the oxygen cylinder and the generator are joined with ordinary rubber tubing. Those in the immediate vicinity, and on the delivery side, of the generator are joined with Koroseal tubing. (The authors are indebted to T. L. Gresham of the B. F. Goodrich Company for a supply of this tubing.) Earlier attempts to use all-glass connections led to excessively rigid equipment.

The dry ozonized gas passes into the end of a tubular glass manifold which distributes the gas stream into the ozonizing tubes through three side arms. (The number of side arms and ozonizing tubes can doubtless be increased and thus be adapted to the requirements.) Each connection between the manifold side arms and the ozonizing tubes is made flexible by inserting a piece of Koroseal tubing. The side arms are equipped with stopcocks, so that each tube may be removed without disturbing the operation. The end of the manifold is equipped with a stopcock, so that the ozone stream may be bypassed. The gas streams issuing from the ozonizing tubes are united in an exit manifold similar to that described, and pass into the laboratory hood.

The ozonizing tubes are held by suitable clamps in an ice-water mixture contained in an insulated rectangular trough equipped with a fitted cover and

a drainage valve. The tubes are made of Pyrex, as shown in Figure 3. The dimensions are such that each tube will contain 100 cc. of liquid when filled to a calibration mark near the midpoint of the neck.

During the run some solvent loss through evaporation takes place, and it is necessary to make up the resulting solution to a definite concentration for the subsequent viscosity measurement. This is accomplished by calibrating each tube at 25°, 30°, and 35° with 159.50 grams of carbon tetrachloride (which occupies exactly 100 cc. at 20°, the temperature of the viscosity measurement).

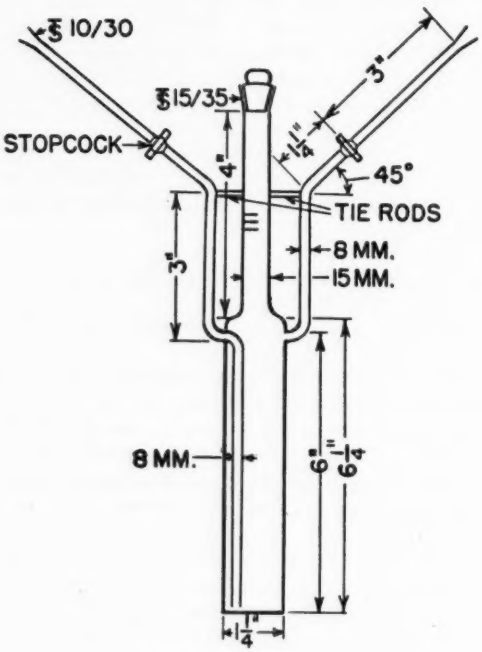

FIG. 3.—Ozonizing tube.

The ozonized contents may then be diluted to exact volume at any known room temperature; visual interpolation is sufficiently exact for intermediate temperatures.

In making a run three solutions are prepared for each lot of Butyl rubber; these are ozonized for 1, 2, and 4 hours, respectively. Samples weighing about 1.5 grams are weighed to the nearest milligram and are dissolved in roughly 40-cc. portions of carbon tetrachloride by tumbling for 48 hours in glass-stoppered containers. Each solution is then transferred to an ozonizing tube, the residual solution being washed in with two 10-cc. portions of the solvent. The tubes are clamped into position in the ice-water mixture and ozonized oxygen is passed through the apparatus at a rate of 10 to 15 cc. per second, the rates through the separate ozonizing tubes being occasionally equalized by adjustment of the stopcocks. The rate of cooling of the solution is sufficiently fast to permit ozonization immediately after immersion of the tubes in the cold bath.

After one hour the first tube is removed from the apparatus, ozonization of the others being allowed to continue for the longer periods. A stream of air is passed through the contents for about 15 minutes to sweep out excess ozone, and after the contents have been allowed to stand at room temperature for a total time of at least 0.5 hour, they are diluted to exact volume with carbon tetrachloride, thoroughly mixed, and the viscosity at 20° determined with a Ubbelohde suspended-level viscometer, proper account being taken of the kinetic energy correction.

TREATMENT OF THE DATA

The ratio of the viscosity of the solution to that of the solvent gives the relative viscosity, η_r; from this and the concentration, c, of the polymer, $[\eta]$ is calculated by Equation 1. Dividing this value by 1.255 (Equation 2), gives the corresponding intrinsic viscosity in diisobutylene. The values thus obtained for the three solutions are plotted against time of ozonization; curves such as are shown in Figure 4 are obtained. The linear portion of the curve,

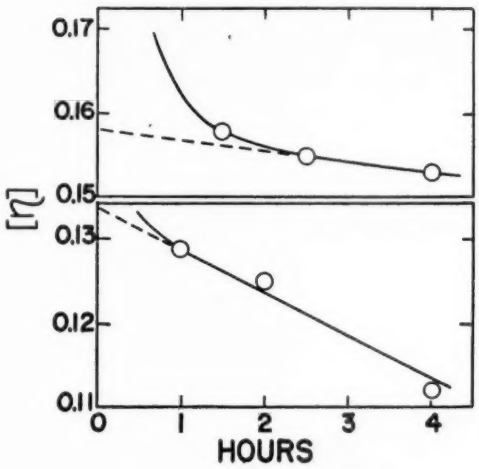

FIG. 4.—Typical ozonization curves.

which usually occurs between the 2- and the 4-hour points, but which occasionally includes the 1-hour point, is extrapolated to zero time. From the intercept the viscosity-average molecular weight, $\bar{M}_v$, of the degraded polymer is obtained from the following relation[3]:

$$\log \bar{M}_v = 5.378 + 1.56 \log [\eta] \tag{3}$$

The number-average molecular weight $\bar{M}_n$ is then given[1] by the relation:

$$\bar{M}_n = \bar{M}_v/1.832 \tag{4}$$

and the unsaturation, U, of the original polymer, expressed as moles of isoprene units per 100 moles of isobutylene units (mole-per cent), follows from

$$U = 5610/\bar{M}_n \tag{5}$$

ALTERNATIVE METHOD OF ESTIMATING *U* FROM IODINE CHLORIDE DATA

For a number of years this laboratory has employed a modification[4] of the Kemp-Wijs method for obtaining comparative unsaturation values for Butyl polymers.

In this routine procedure a 0.3-gram sample of the rubber is dissolved in 100 cc. of carbon tetrachloride, 5 cc. of 0.2 *N* Wijs reagent is added, and the mixture is allowed to stand in the dark for 1 hour at room temperature. Twenty cubic centimeters of 15 per cent alcoholic potassium iodide are then added, the mixture is titrated with 0.1 *N* thiosulfate to a canary yellow color, 5 cc. of 0.5 per cent starch solution are added, and the titration is completed. A blank determination is made simultaneously, and from the difference in the titers the unsaturation value *U*(ICl), in mole-per cent, is calculated from the formula:

$$U(\mathrm{ICl}) = 0.281 \times (\text{cc. of } 0.1\ N \text{ thiosulfate})/\text{grams of sample} \qquad (6)$$

It has been found invariably that these values are approximately twice as large as those obtained by the ozonolysis method, and it has been suggested[1] that the difference is due to factors, such as substitution reactions, commonly encountered in iodine chloride determinations. Figure 5 shows the relation-

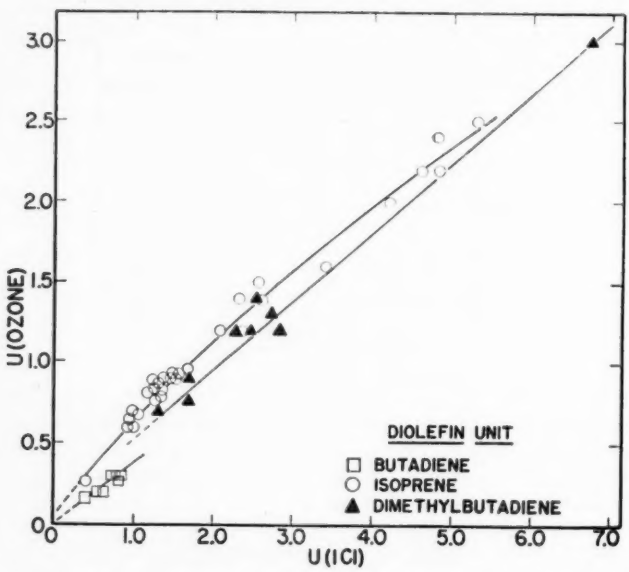

FIG. 5.—Correlation of unsaturation values for butyl rubbers containing various diolefin units.

ship between the two values of *U* for a number of Butyl rubber samples of varying degrees of unsaturation. The curve for the isoprene copolymer was plotted from a quadratic equation by the method of least squares. With the aid of this graph it is possible to obtain at least approximate values of *U* from corresponding values of *U*(ICl) determined by the method described above. More recently Kemp and Peters[5] have published an iodine chloride procedure

for Butyl rubber in which a different solvent and different reaction conditions are employed. It is likely that their method would be capable of similar use in estimating U by this indirect method.

It was considered of interest to include in Figure 5 curves for Butyl polymers containing butadiene and dimethylbutadiene, respectively, as the diolefin units. Over the unsaturation ranges investigated, these materials show linear relationships between U (ozone) and U (ICl), although the slopes differ by about 20 per cent. In view of the well-known influence of substituent groups on the course of the reaction of an olefin with halogens, these differences are not surprising.

ACKNOWLEDGMENT

The writers are indebted to some of their associates who synthesized the special polymers used in part of this work.

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IDENTIFICATION OF RAW AND VULCANIZED RUBBERLIKE POLYMERS. II. DETERMINATION OF SWELLING RATIOS *

L. F. C. PARKER

The identification of rubberlike polymers by determining the reaction time in a mixture of nitric and sulfuric acids was dealt with in Part I[1] of this series.

Previous work, carried out in the laboratories of the Research Association of British Rubber Manufacturers, has shown that the ratios of swelling in different liquids are different for different types of "rubber", hence this suggests a method of indentification based on the estimation of these ratios. Results of this previous work have shown that benzene, light petroleum (b.p. 40–60°), and aniline are suitable liquids, and experience with these has shown the method to be sound in principle and useful in practice.

So far as can be ascertained from the data available, the present experimental results are in accord with the theory developed by Gee[2] to explain the swelling of rubberlike polymers in liquids. This theory may be able to indicate the lines along which further improvements of the method should be sought.

The method has been referred to by Stern[3], and has been described in a memorandum on identification of rubbers issued by the Ministry of Supply[4].

EXPERIMENTAL PROCEDURE

The swelling ratios of a vulcanizate are determined as follows. Three test-specimens are cut from the sample; these are preferably flat discs or rectangles of about 2 sq. cm. area, and should not be more than about 0.25 cm. thick, otherwise the period required for absorption of liquid becomes undesirably long. The specimens are extracted in acetone for at least 16 hours, using a Soxhlet type of apparatus, and then dried to constant weight at 100° in air, or preferably (to avoid oxidation and/or cross-linking) in a vacuum or inert gas at a moderate temperature. The specimens are then totally immersed, one in each of the three swelling liquids, *viz.*, benzene (*B*), light petroleum (aromatic-free, b.p. 40–60°) (*P*), and aniline (*A*), kept at a constant temperature of 25° C for seven days, after which the specimens are removed from the liquids and the surfaces dried by a suitable absorbent material, such as filter paper. The weights of the swollen specimens are recorded.

"Swelling" is defined as volume of absorbed liquid expressed as a percentage of the volume of the rubber specimen after extraction with acetone and drying; it is given by the formula: $[(W_2 - W_1)R/W_1L] \times 100$, where W^2 = weight of acetone-extracted and dried rubber specimen, W_2 = weight of swollen specimen, R = specific gravity of the rubber, and L = specific gravity of liquid used. In practice the specific gravity of the rubber before extraction is used in the above formula; this gives an approximate value for the swelling (the exact value would be given by using the specific gravity after extraction).

* Reprinted from the *Journal of the Society of Chemical Industry*, Vol. 64, No. 3, pages 65–67, March 1945.

When calculating the swelling ratios, however, the specific gravity of the rubber cancels out, so that no error is involved.

There are six possible swelling ratios, *viz.*, B/P, P/A, A/B, and their reciprocals, where B, P, and A are the swellings in benzene, light petroleum, and aniline, respectively. A single ratio will often give a good indication of the nature of the sample, but more reliable results are obtainable by using two ratios; B/P and B/A have been found the most useful in practice. By plotting log (B/P) against log (B/A) for known types of rubber, a graph similar to Figures 1 and 2 is obtained; as the ratios for a given type vary slightly, each

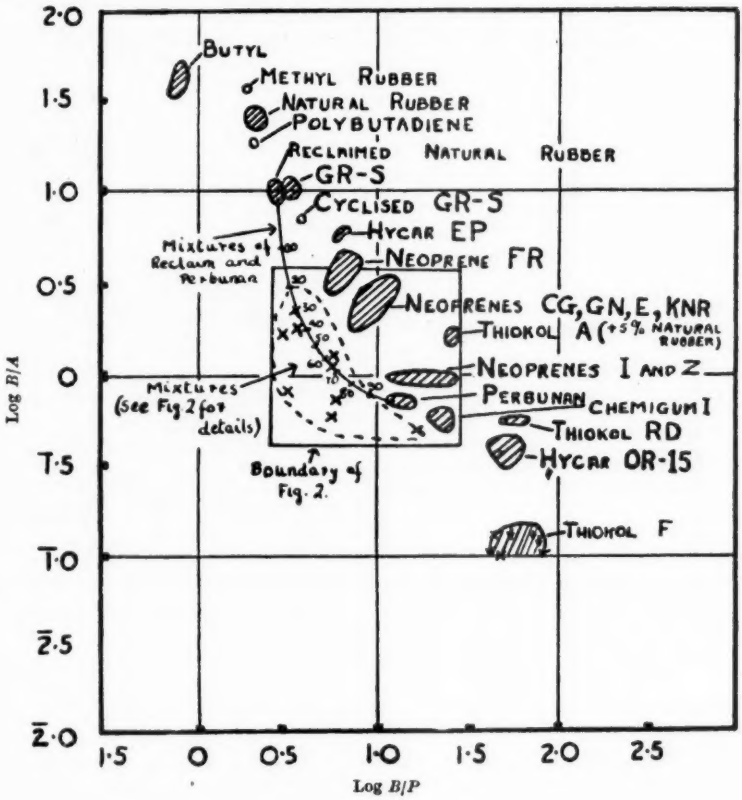

FIG. 1

type is shown in these figures by a shaded area representing the observed extent of variation. The position, on such a graph, of the point for an unknown sample indicates the type of rubber present, provided it is not a mixture of two or more types. A positive method cannot as yet be given for mixed rubbers unless a knowledge of the qualitative analysis of the sample is obtained. Results that have been obtained on certain mixtures are discussed later in this paper.

REMARKS ON EXPERIMENTAL PROCEDURE

It is important that the specimens be extracted with acetone before swelling, this removes softeners, "extenders", and similar materials. Failure to

extract these at this stage enables the swelling liquid to dissolve out these substances and hence give an apparent swelling less than the true value. Where the true swelling is small, the percentage error due to extraction by the swelling liquid can be very large, and may even cause the calculated "swelling" to be negative.

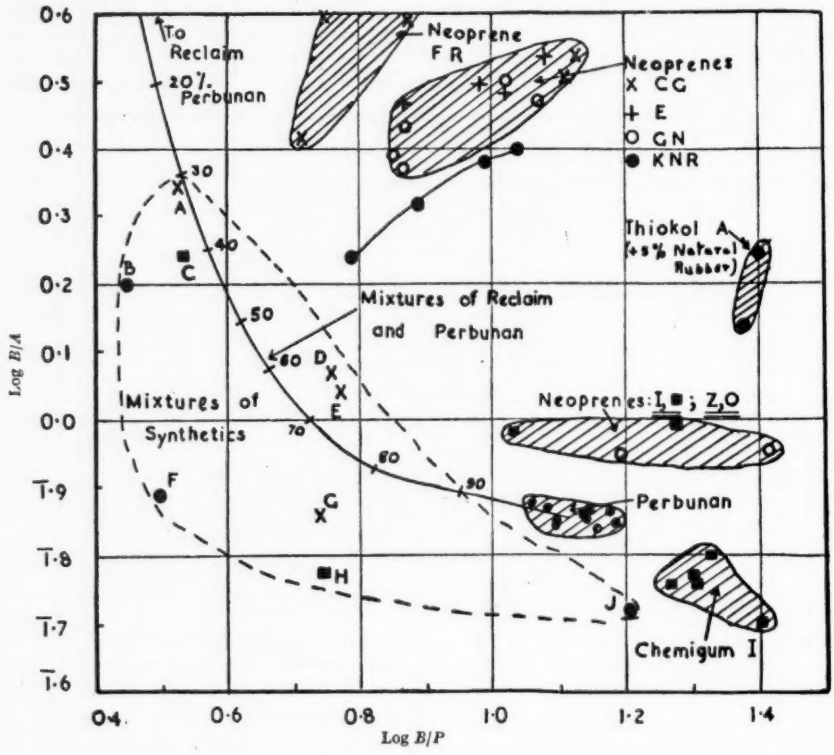

FIG. 2

In this work a seven-day immersion period was standardized. The use of one fixed immersion period does not give an exact measure of the swelling capacity of a liquid for a rubber, but exact results can be obtained by determining the swelling after various immersion periods, and interpreting the results graphically in the manner described by Scott[5]. This procedure might be advantageous if the possibility of obtaining finer distinctions between rubbers were being investigated, but the use of a single immersion period has proved adequate for the present purpose.

SWELLING RATIOS OF NATURAL AND SYNTHETIC RUBBERS

VULCANIZATES CONTAINING ONE TYPE OF RUBBER ONLY

The ratios B/P and B/A have been determined for vulcanized samples of natural rubber and the principal types of synthetic rubber. From each type several samples of different composition were examined. These were compounded and vulcanized generally in accordance with normal technical prac-

tice, but were deliberately made to represent a wide range of variation in composition. The filler was usually carbon black, in proportions ranging up to 100 parts by weight per 100 parts of the rubber, the types used including fine thermal, semireinforcing furnace, and medium and easy-processing channel blacks. A few of the rubbers contained as filler either whiting or a "reinforcing" calcium carbonate. Plasticizers such as pine tar, bitumen, dibutyl phthalate, tricresyl phosphate, and dibenzyl ether, in proportions ranging up to 30 parts per 100 of rubber, were used in many of the mixes. All the mixes were vulcanized approximately to the optimum, as judged by tensile properties.

It was found that, for any given type of rubber, the actual swelling increases more or less regularly with increasing B.S. hardness number, *i.e.*, as the vulcanizate is made softer; this agrees with previous results[5], but the B/P and B/A ratios remain substantially constant in spite of variation in hardness or composition; it is this approximate constancy that gives the ratios their value as a means of identification.

TABLE I

SWELLING RATIOS FOR MIXTURES OF RUBBERS

Mixture	Type of mixture*	B	P	A	B/P	B/A
A	Perbunan, 33 vols. Reclaim, R.H.C. 67 vols.	190	57.6	85.8	3.3	2.2
B	Natural rubber, 64 vols. Thiokol-A, 36 vols.	96.1	27.8	45.5	3.5	2.1
C	Hycar OR-15, 31 vols. Reclaim, R.H.C. 69 vols.	175	51.7	102	3.4	1.7
D	Perbunan, 63 vols. Tire crumb, R.H.C. 37 vols.	305	53.8	261	5.7	1.2
E	Perbunan, 67 vols. Reclaim, R.H.C. 33 vols.	181	30.8	165	5.9	1.1
F	Thiokol-F, 58 vols. Tire crumb, R.H.C. 42 vols.	180	57.3	232	3.1	0.78
G	Perbunan, 63 vols. Thiokol-A, 37 vols.	47.3	8.4	65.1	5.6	0.73
H	Hycar OR-15, 67 vols. Reclaim, R.H.C. 33 vols.	144	26.0	239	5.5	0.60
J	Perbunan, 56 vols. Thiokol-F, 44 vols.	111	10.6	215	10.5	0.52

* R.H.C. = Rubber hydrocarbon content.

In Figures 1 and 2, log (B/P) is plotted against log (B/A), and each group of rubbers falls within the appropriate shaded area (Figure 2 is an enlargement of a portion of Figure 1); from Figure 1 it can be seen that the shaded areas representing vulcanizates consisting of only one type of rubber lie approximately on a straight line, an interesting result which is discussed further in the next section.

In the case of Thiokol-F, the area in Figure 1 is not complete, because the samples tend to disintegrate in aniline, and the B/A ratio is probably smaller than is shown, the swelling in aniline being very large, *e.g.*, 1000 per cent. In some cases the actual swellings may be difficult to measure, especially in light petroleum, where the value is about 0.3 per cent for Thiokol-A, although it may sometimes be quite large, for example 200 per cent with Butyl. Swelling values in aniline may lie between (say) 3 per cent for Butyl and 1000 per cent

for Thiokol-F, while swelling values in benzene lie between (say) 7 per cent for Thiokol-A and 400–500 per cent for several rubbers.

MIXTURES OF SYNTHETIC RUBBER WITH NEW OR RECLAIMED NATURAL RUBBER

The vulcanizates for which results are given in Table I each consist of two different types of rubber in the proportions (by volume) indicated. The reclaim used was natural-rubber, whole-tire reclaim, and the tire crumb was natural-rubber tire-tread ground to pass a 20-mesh sieve.

The logarithms of these swelling ratios have been plotted in Figures 1 and 2. They are shown by crosses in Figure 1 and by the mixing letter in Figure 2. The curve joining the areas for reclaim and Perbunan is the curve representing mixtures of these two calculated on the assumption that individual swelling values for the mixtures are linearly related to the values for the two ingredients; owing to the use of logarithms in Figures 1 and 2, a curve and not a straight line is obtained. The point A lies near the calculated 33/67 and E near the 67/33 Perbunan/reclaim points on the curve. Hence if the types of rubber in a mixture and their swelling ratios are known, it may be possible to determine proportional concentrations in an unknown sample. The presence of a mixture, moreover, is normally suggested by the point falling to the left of the line through the positions representing vulcanizates containing one type of rubber only (see also next section in this connection).

THEORETICAL CONSIDERATION OF SWELLING RATIOS

The most complete theory of the swelling of rubber in various liquids is that due to Gee[2]. According to this theory swelling is a function of $\sqrt{V_0}[\sqrt{(E_0/V_0)} - \sqrt{(E_r/V_r)}]$, where V_0 and V_r are the molar volumes of the liquid and rubber, respectively, and E_0/V_0 and E_r/V_r are their respective "cohesive energy densities" (C.E.D.); E_0 is a function of the molar latent heat of evaporation of the liquid, and E_r is a hypothetical equivalent quantity for the rubber. Swelling is a maximum when $[\sqrt{(E_0/V_0)} - \sqrt{(E_r/V_r)}]$ is zero, that is, when the rubber and the liquid have the same C.E.D.

This principle was used by Gee to determine empirically the C.E.D. of vulcanized rubber. Measurements were made of the swellings in various liquids of known C.E.D., the liquid in which the swelling was a maximum having a C.E.D. approximately equal to that of the rubber.

According to Gee's theory the swelling (Q) equals $Me^{-\beta V_0(d_0-d_r)^2}$, where $d_0 = \sqrt{(E_0/V_0)}$ and $d_r = \sqrt{(E_r/V_r)}$; M is a constant for liquids of the same chemical type, and often, but not always, for those of different types; β may vary with $(d_0 - d_r)$ for a given rubber, and may also vary from one rubber to another.

Considering a given rubber, we thus have for the swelling in three liquids a, b, and c: $Q_a = M_a e^{-\beta_a V_a(d_a-d_r)^2}$; $Q_b = M_b e^{-\beta_b V_b(d_b-d_r)^2}$; $Q_c = M_c e^{-\beta_c V_c(d_c-d_r)^2}$, where M_a, M_b, and M_c are the values of M for the given rubber in the three classes of liquids represented by a, b, and c; β_a, β_b, and β_c are different because of the different values of the quantities in brackets.

The above equations give:

$$\log(Q_a/Q_b) = \log(M_a/M_b) + d_r^2(\beta_b V_b - \beta_a V_a) - 2d_r(\beta_b V_b d_b - \beta_a V_a d_a) + \beta_b V_b d_b^2 - \beta_a V_a d_a^2$$

$$\log(Q_b/Q_c) = \log(M_b/M_c) + d_r^2(\beta_c V_c - \beta_b V_b) - 2d_r(\beta_c V_c d_c - \beta_b V_b d_b) + \beta_c V_c d_c^2 - \beta_b V_b d_b^2$$

Further development of these equations to give the relation between $\log (Q_a/Q_b)$ and $\log (Q_b/Q_c)$ for any given set of three liquids requires more complete knowledge of the constants β, M, and d than exists at present.

It can be shown, however, that under certain simple sets of conditions which could be more or less nearly realized in practice (*e.g.*, M_a/M_b and M_b/M_c equal to unity, or independent of the rubber, and either $\beta_a V_a = \beta_b V_b = \beta_c V_c$ or $\beta_a V_a d_a = \beta_b V_b d_b = \beta_c V_c d_c$) the relation between $\log (Q_a/Q_b)$ and $\log (Q_b/Q_c)$ for different rubbers is represented by a straight line, the position of a rubber on this line depending simply on its C.E.D. This agrees with the experimental observation that the various rubbers lie roughly on a straight line on the $\log (B/P)$:$\log (B/A)$ graph. Moreover, a mixture of two rubbers would be expected to give a more widely spread C.E.D.-swelling curve; this is equivalent to having a smaller value of β, assuming the curve to be still approximately of the "normal" type. It can be shown that, under the particular conditions postulated above, this results in the point for the mixture on the log-log graph being nearer to the origin than the line representing single rubbers. This again appears to be the case according to the experimental data (see Figure 1).

It is thus seen that, although full agreement between theory and experiment has not been demonstrated, the theory, under certain restrictive conditions, explains the observed data.

SUMMARY

The ratios of the swellings of vulcanized rubberlike polymers in benzene, light petroleum (b.p. 40–60°), and aniline, at 25° C, have been found to be different for different polymers, but to be within a well-defined narrow range for each polymer, and the ratios substantially independent of the state of vulcanization and nature and proportion of the fillers. Hence the ratios for an unknown sample may be utilized in its identification, preferably by plotting the values on a graph showing the ratios for the common types of rubberlike polymers.

ACKNOWLEDGMENT

Acknowledgment is made to the Ministry of Supply and to the Research Association of British Rubber Manufacturers for permission to publish this paper, and of the assistance given by L. Mullins and J. R. Scott in connection with the last section.

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THE WEBER COLOR TEST FOR THE IDENTIFICATION OF NATURAL RUBBER*

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The Weber color reaction[1], mentioned in a recent note[2], has become of importance in detecting natural rubber in mixtures in which it may be considerably diluted with synthetic rubber or nonrubber materials. The detailed instructions for carrying out the test are given elsewhere[3], and Stern[4] has published a table which shows also the colors obtained when the test is applied to rubbers other than the natural product. It is clear from this table, and is confirmed by our experience, that the strong violet color developed is distinctive for natural rubber and gutta-percha, provided that the material has been extracted with acetone. However, color reactions in organic chemistry are rarely found to be as specific as earlier workers have claimed, and work is being carried out in these laboratories to establish the limitations of the reaction when applied to rubberlike materials.

With very few exceptions, synthetic rubbers and rubberlike materials available at present do not give a positive result with this test, although very faint violet colors, which cannot be confused with a positive result, are sometimes obtained. Those giving any violet color are listed in Table I.

TABLE I

Material	Nature of the material	Result of test
Methyl rubber	Polymer of 2,3-dimethylbutadiene	Strong violet, as for natural rubber
Neoprene-FR	Copolymer of chloroprene with second component	Strong violet, as for natural rubber
Gutta-percha and balata	Polyisoprenes, isomeric with natural rubber	Strong violet, as for natural rubber
Butyl-B	Copolymer of isobutene and 1.5% isoprene	Very faint violet color
Pliofilm	Natural rubber hydrochloride	Very faint violet color
Buna-85	Polybutadiene	Very faint violet color (some samples only)

Cyclized and vulcanized natural rubbers (including ebonite) give a positive reaction, but other modified rubbers, *e.g.*, chlorinated rubber, rubber nitrate and rubber hydrochloride, give a negative or faint result.

Examination of Isoprene Derivatives.—The liquid obtained from the dry distillation of rubber contains considerable quantities of isoprene, but it gave no violet color until it had been heated under reflux for an hour. The intensity of the color increased on standing or after continued heating. Isoprene prepared in the laboratory from acetone *via* a Grignard reaction similarly showed a negative reaction until it had been heat-polymerized. Bay oil, containing myrcene, a linear dimer of isoprene, gave the violet color, but only after the brominated compound had been left in contact with phenol overnight, while turpentine (containing cyclic isoprene derivatives) did not give the violet color, even after heating.

* Reprinted from the *Analyst*, Vol. 70, No. 830, pages 175–176, May 1945.

Nature of the Reaction.—Brominated rubber was prepared by bromination below 0° C, in presence of a trace of alcohol. This treatment has been shown by Bloomfield[5] to give a compound in which all the bromine is taken up at the double bond. The bromination was carried out in carbon tetrachloride solution, and phenol, also dissolved in carbon tetrachloride, was added. No color was obtained on warming. Another sample of brominated rubber was prepared by the use of *N*-bromosuccinimide, bromination being thus restricted to substitution in the alpha position. This compound gave the usual color on warming in carbon tetrachloride solution with phenol. Bromination of the methylene group alpha to the double bond in a polyisoprene thus seems essential for the production of the violet color on warming with phenol. In methyl rubber this essential structure exists, whilst modifications of natural rubber produced by vulcanization or cyclization involve only a proportion of the monomer units. Chlorination, hydrochlorination and nitration are more drastic and involve most, if not all, of the monomer units, either by addition at the double bond, or substitution, or, most probably, in commercial samples a mixture of both forms of attack; these do not give the color. The reaction is, therefore, probably specific for an activated alpha methylene group. In natural rubber this activation is achieved by means of the methyl group.

Exceptions.—As already mentioned, a very faint color has been obtained with some samples of Buna-85, some samples of a rubber hydrochloride (Pliofilm), and Butyl-B, a copolymer of isobutene with small amounts of isoprene. The color with the Pliofilm can be accounted for by supposing that some monomer units of the original rubber remain unattacked, but that arising from Buna-85, is, at present, unexplained but may arise from the occurrence of 1,2-addition of butadiene. This faint color cannot, however, be mistaken for the positive result given by even very small amounts of natural rubber. Neoprene-FR is a copolymer of chloroprene and an undisclosed second component. Wet oxidation of the material gives some acetic acid[2], and it is reasonable to suppose that isoprene is a unit of the copolymer. The necessity for prior extraction with acetone in any doubtful test is stressed because positive indications are obtained with certain nonpolymeric materials, of which linseed oil is an example. Here, the methylene group between the two double bonds in linoleic acid is known to be especially reactive. Cyclopentadiene, also containing methylene-interrupted double bonds, reacts in the same way, with formation of a colored compound. We are indebted to G. H. Wyatt for drawing our attention to the fact that the Weber reaction is strikingly similar to the Halphen-Hicks reaction for rosin, and there can be no doubt that a very similar mechanism is responsible, since rosin will give a color under the conditions of the Weber test, but the color is produced immediately, is of a different shade, and rapidly turns brown. Confusion is, therefore, impossible and, in any event, rosin (which is frequently used in Neoprene compounds) is acetone-soluble and would be extracted.

Natural rubber reclaimed by the alkali process fails to give the reaction, nor could it be restored by treatments ranging from mild washing to autoclaving with hydrochloric acid. It is hoped to deal elsewhere with the implications of this.

Conclusions.—The Weber color reaction appears specific for an active methylene group next to a double bond, such as is in the grouping —CH^2—C=C^{CH^3}

which occurs in linear polyisoprenes, of which natural rubber is the best known example. The grouping occurs also in methyl rubber and in copolymers containing isoprene. In analytical practice it is useful for identifying natural rubber (except as alkali reclaim), although caution must be used where an isoprene copolymer is likely. Further work is in progress with a view to substantiating these conclusions and to establishing the mechanism of the reaction.

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COAGULATION STUDIES OF THE LATEX OF *CRYPTOSTEGIA GRANDIFLORA, R. BR.* A WARTIME SOURCE OF VEGETABLE RUBBER. I*

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This work was undertaken at the request of the Department of Supply with a view to evolving a method which would not require heavy expenditure of chemicals and would be workable by the same equipment used as in the case of *Hevea*. With these objects in view information has been collected with special reference to the hydrogen-ion concentration of the latex. The details of the methods are given in the experimental procedure.

Coagulation by Chemical Reagents.—Under this head are described the results of mineral and organic acids, alkalies, organic bases and salts, and also chemical reagents used for coagulating proteins and those which bring about hydration and dehydration. It was found that acids can coagulate the latex in a range which requires very small quantities of coagulant, and that, with increase in acidity, the yield of coagulum decreases. In most cases if the acidity reaches the limit which would drop the pH of the latex from 4.6 to 4.0, the latex does not coagulate. Thus with a decrease of 0.6 in the pH value, the latex is stabilized. Mineral and organic acids appear to be equally good, and the coagulum produced has good tensile strength and elasticity and can be sheeted. Organic acids from formic to butyric acid with an increase in the number of carbon atoms have no special advantage. The minimum quantities of acids effective to coagulate a liter of latex are given in Tables I and VIII[1].

When coagulation is effected with alkalies, the minimum quantity of reagent necessary is that which raises the pH to 7.7. If the concentration is less there is a partial coagulation, and if it is more, the latex turns into a pasty mass. In coagulation with alkalies there is the advantage that the process can be completed in a very short time, whereas in the case of acids it is necessary to keep the latex overnight. Alkali coagulation has demerits as well. The coagulum is very spongy and has a poor tensile strength and elasticity compared to coagulum obtained by acid coagulation. Further, the coagulum develops tackiness[2] and this depends further on washing and temperature. If the coagulum is washed till it is free of its alkalinity and is dried at low temperature (70–80°), the tackiness becomes less. This faulty coagulation can be corrected to a great extent if the coagulum is dipped in a 1 per cent solution of mineral and organic acids before washing.

With bases (quinoline, aniline, toluidine and pyridine) 0.2 to 1 cc. of the base brought about effective coagulation of 10 cc. latex. Smaller quantities of quinoline, aniline and toluidine could not be used, owing to immiscibility of the bases with water. It was studied only with pyridine, and it was noticed

* Reprinted from the *Journal of the Indian Chemical Society*, Vol. 21, No. 6, pages 191–214, June 1944.

that 1 cc. of 0.5 per cent solution of pyridine in tap water coagulated 10 cc. of latex. The coagula emit an odor of the base, which is not removed even on washing with water and alcohol. The pH value of the serum obtained after coagulation with bases could not be determined, but with 0.5 per cent pyridine solution there was a gradual increase from 4.6 to 5.4 on increasing the volume of coagulant from 1 to 10 cc. In the case of alkalies it was pointed out that, with increased alkalinity, the latex turned into a pasty mass, but with bases this behavior was not observed.

TABLE I

COAGULATING EFFECT OF VARIOUS SUBSTANCES

Coagulant	Number of grams per liter of 30% Hevea latex, with names of authors				Quantities per liter of 2–7% *Cryptostegia* latex by Siddiqui
	Eaton	Morgan	Parkin	Beadle and Stevens	
Acetic acid	1.0	1.0	9.5	1.5–6.0	0.25–4 cc.
Formic acid	0.6	0.8	4.5	—	0.25–2 cc.
Hydrochloric acid	0.7	0.7	1.0	0.4–0.5	0.25–1 cc.
Hydrofluoric acid	0.5	0.5	—	—	0.5 –2 cc.
Nitric acid	1.0	1.0	3.0	—	0.1 –0.2 cc.
Sulfuric acid	0.9	1.0	1.0	0.5–10	0.5 –0.4 cc.
Calcium chloride	5.0	5.0	—	—	0.05–0.25 g.
Ammonium sulfate	10.0	10.0	—	—	0.05–0.25 g.
Tannic acid	1.0	1.0	—	—	1.0 g.
Oxalic acid	2.0	—	—	—	0.5–1.2 g.
Tartaric acid	2.5	—	—	—	0.5–2 g.
Citric acid	5.0	—	—	—	0.5–2 g.

The action of acids and alkalies shows that latex has got a stability range from 4.2 to 7.5 or 7.7. At the extremes complete coagulation of the latex takes place, but below 4.0 the latex passes into a second zone or phase. That alkalies are to be avoided for coagulation finds further support from a statement of Stevens and Stevens: "As a rule caustic soda should be avoided for latex manipulation, as under certain conditions the resulting rubber tends to soften and becomes tacky (sticky), due to some obscure type of chemical decomposition."

Salts can be used for the coagulation of latex and very small quantities are required. Good results were obtained with calcium and sodium chlorides, aluminum and ammonium sulfates, and alum.

Coagulants for proteins were also used, and they too coagulated the latex, but the concentrations used were not very effective and the coagula produced by picric and tannic acids were colored. Alcohol and acetone alone also brought coagulation, and the same result was achieved by common dehydrating agents.

Formaldehyde, lemon juice, curd, molasses and serum itself coagulated latex, and so shortage of chemicals is no consideration in the coagulation of latex.

Water Coagulation.—Coagulation can be effected by adding latex to six volumes of hot water, while five volumes brings about partial coagulation and four volumes produces flocculation. The dilution varies from season to season with the percentage of rubber; it is less when the percentage of rubber is high and more when it is less, especially during the defoliation period. The pH value also depends on the dilution. If cold water is added dropwise till a clear straw colored serum is obtained, the pH rises to 7.5, but coagulation can also

be brought about at a low pH value when six or seven volumes of hot water are used.

Autocoagulation and Autocreaming.—When latex is allowed to stand quietly at room temperature (25–31°) for a day or two, the suspended particles float to the surface, leaving below a clear reddish brown serum. This stage is characterized by the fact that particles do not coalesce, and on stirring or shaking disperse again in the serum. At this stage it is possible to separate the flocculated mass from the serum, which can be made richer in rubber content and the particles of which can be coalesced by washing with water or by filtration. When the latex is allowed to stand for a week or so at room temperature, the particles of cream unite together and form a clot of rubber having a junketlike appearance. Both of these methods can be used for the coagulation of latex on a large scale. The pH value drops from 4.6 to 4.2.

Coagulation by Heat.—Latex can be coagulated by natural heat or by artificial heat (dry heat, moist heat and smoking). This process will have an important bearing if the whole rubber is to be obtained from the latex.

Coagulation by Centrifuging and Shaking.—This method can be used on a large scale. The coagulum separates and floats to the surface. A part of the coagulum remains in the serum, which can be recovered on dilution. The pH value of the latex remains unchanged.

Coagulation by Electric Current.—When the current from a battery is passed through latex, rubber particles move towards the anode, and produce a change in the hydrogen-ion concentration of the latex. The observed pH was 3.8.

Broadly speaking the methods of coagulation can be divided into two classes. (1) Chemical methods, which involve the use of chemicals which are added to the latex either from outside (coagulation by chemical reagents and water, coagulation by smoking) or which are formed within the latex due to changes brought about by enzymes, microörganisms, electric current or some unknown cause (autocoagulation and coagulation by electric current). The chemical process is always accompanied by a change in the hydrogen-ion concentration, which ranges from 4.2 to 7.5. (2) Physical methods, which do not involve the use of chemicals (coagulation by dry heat, by centrifuging and shaking) and whereby no change is brought about in the hydrogen-ion concentration of the latex.

Explanations for the coagulation of latex will form part of a separate communication.

EXPERIMENTAL

COAGULATION BY CHEMICAL REAGENTS

(1) *General Methods of Coagulation by Acids and Salts.*—To the latex is added the required quantity of the acid or the salt solution, and the mixture is warmed at 90° for five minutes after keeping overnight at room temperature (25–27°). The coagulum is separated, sheeted, washed well in running water, dried at 90–95°, and weighed. This dry rubber is known as D.R.C. (dry rubber content).

(2) *General Method of Coagulation by Alkalies and Bases*[3].—On adding the required quantity of an alkali or an organic base to latex, the latter turns yellow or pink. The mixture is warmed for five minutes at 90°. On stirring with a glass rod a white coagulum and a clear yellow or reddish brown serum are obtained. The coagulum is sheeted and, after washing well with water till it is free of alkali, it is dried at 90–95° in an air-oven.

(3) *Difference Between the Coagula Obtained by the Above Two Methods.*—In coagula obtained by method (1) the fibres of rubber unite and form a tough and tenacious close meshed network. The texture is hard and some time is required for sheeting. The tensile strength is great, and the elasticity is good. The coagulum obtained by method (2) is of a different nature altogether. It is a highly spongy mass, in which the mesh is open and the fibres or threads do not form one compact tough structure. The coagulum can be spread enormously, but is extremely poor in tensile strength. It breaks easily and has poor elasticity.

Correction of the Faulty Coagulation.—If the coagulum obtained by method (1) is washed and is given a dip in 1 per cent solutions of hydrochloric, sulfuric and acetic acids for 15 minutes, it becomes white and resumes the tensile strength and elasticity. Before drying it should be washed well with water. On drying, tackiness still persists to a slight extent.

COAGULATION BY ACIDS

Preliminary observations showed that increased acidity, which decreases the pH value of the latex from 4.6 to 4.0, also decreases its percentage of dry rubber content (D.R.C., 111). This inference helped in fixing the concentration of the acid solution, and the following was the procedure adopted. Prepare a dilute solution of the acid, add in portions of 1 cc. to latex (10 cc.) and note the pH value after each addition till it reaches 4.0. If 1 cc. of any solution decreases the pH to 4.0, the acidity is very high, and it is reduced to such an extent that at least 4 or 5 cc. is required to lower the pH to 4.0. With most of the acids, 1 per cent solution was found effective for coagulating the latex, but hydrochloric, sulfuric, nitric and boric acids gave good results with 0.25, 0.2, 0.2 and 0.1 per cent solutions, respectively. After fixing the concentration of the acid solution, its coagulating power was further studied by adding 1, 2, 3, 4, 5 and 6 cc. to 6 portions of latex (10 cc.) and determining the D.R.C. The concentration of the solution was then halved, and five more determinations of D.R.C. were made. The range of acidity of the two solutions helped in deciding the minimum and maximum quantity of the coagulant that would bring about effective coagulation of the latex. In the following tables 10 cc. of the latex were used for each observation, and the white coagula could be sheeted, and had good tensile strength and elasticity. The indicator was bromocresol green unless otherwise mentioned. D.R.C. values throughout this investigation are compared with D.R.C. obtained by coagulating an equal volume of latex with water because it coagulates the latex completely as mentioned elsewhere, and is shown in the tables as standard. The solutions of the acids were prepared with tap water. Results appear in Table II.

Results with acetic acid and oxalic acid solutions are presented in Table IIB. For mixtures with alcohol the following procedure was adopted. To latex (20 cc.) were added 1 cc. of 1 per cent solution of acetic acid and 10 cc. of alcohol drop by drop, whereby a white coagulum and a reddish brown, turbid serum with pH 4.6 were formed. The D.R.C. weighed 1.1986 grams (5.99 per cent). The effect of alcohol was studied further. Observations are recorded in Table IIB.

TABLE IIA

COAGULATING EFFECT OF INORGANIC ACIDS

Hydrochloric acid

Hydrochloric Acid[4].—With 0.5 per cent solution two sets of experiments were done. In one the acid was mixed with latex and warmed in boiling water for 10 minutes and, after keeping overnight, was again warmed. In the second set the mixture was warmed only once after keeping overnight. It was found that warming after keeping overnight was better. In the first set of experiments there was flocculation, but the flocks did not coalesce. Experiments 1 and 2 gave coagula, but in other cases increased acidity failed to produce any coagulum. From the second set it is clear that 1 cc. of the acid solution containing 0.005 cc. of hydrochloric acid brought about coagulation of 10 cc. latex to the extent of 94 per cent and 0.025 cc. acidity decreased it to 15 per cent. Therefore the concentration of the acid solution was halved, and 0.24 per cent solution (2.5 cc. concentrated acid in a liter of tap water) gave good results which showed that 0.025 cc. of hydrochloric acid can bring about coagulation of 100 cc. of latex. In the case of Hevea the required acidity is 0.04–0.05 per cent.

	(1) With 0.5% solution. Mixture warmed before and after keeping overnight (first set)			(2) With 0.5% solution. Mixture warmed only once after keeping overnight (second set)			(3) With 0.25% solution		
Volume of coagulant (cc.)	Appearance of serum	pH	Percentage D.R.C. on volume basis	Appearance of serum	pH	Percentage D.R.C. on volume basis	Appearance of serum	pH	Percentage D.R.C. on volume basis
1	Milky	4.4	0.99	Turbid black	4.6	4.08	Dark and slightly turbid	4.4	4.76
2	Milky	4.3	1.03	Turbid black	4.4	3.97	Dark and slightly turbid	4.3	4.68
3	Milky	4.2	0.53	Milky	4.3	0.30	Dark and slightly turbid	4.2	4.15
4	Milky	4.1	0.82	Milky	4.2	0.51	Milky	4.1	0.88
5	Milky	4.0	0.65	Milky	4.0	0.66	Milky	4.0	—
6	Milky	3.9	—	—	—	—	—	—	—
Standard	—	—	—	Milky	—	4.46	—	—	4.91

Hydrobromic acid

(Best results are obtained with an acidity ranging from 0.005–0.003 cc. per 20 cc. latex)

	(1) With 1% solution			(2) With 0.5% solution		
1	Clear, deep dark	4.5	4.36	Clear, deep dark	4.5	4.27
2	Clear, deep dark	4.5	4.41	Clear, deep dark	4.5	4.41
3	Clear, deep dark	4.4	4.20	Turbid, deep dark	4.5	4.07
4	Turbid, deep dark	4.4	4.04	Turbid, deep dark	4.5	3.84
5	Turbid, deep dark	4.4	3.62	Turbid, deep dark	4.5	3.76
6	Turbid, deep dark	4.4	1.99	—	—	—
Standard	—	—	—	—	—	4.49

Hydriodic acid

(Good results were obtained with 0.005–0.030 cc. acid per 10 cc. latex)

	(1) With 1% solution			(2) With 0.5% solution		
1	Dark brown, turbid	4.4	2.12	Dark brown, turbid	4.4	4.50
2	Dark brown, turbid	4.2	2.07	Dark brown, turbid	4.4	4.37
3	Dark brown, turbid	4.0	1.50	Dark brown, turbid	4.3	4.32
4	Milky	—	—	Dark brown, turbid	4.3	4.34
5	—	—	—	Dark brown, turbid	4.2	4.13
Standard	—	—	—	—	—	4.49

TABLE IIA—*Continued*

Volume of coagulant (cc.)	Appearance of serum	pH	Percentage D.R.C. on volume basis	Appearance of serum	pH	Percentage D.R.C. on volume basis
			Hydrofluoric acid[5]			
			(0.005–0.02 cc. coagulated 10 cc. latex effectively)			
	(1) With 1% solution			(2) With 0.5% solution		
1	Brownish red, turbid	4.4	6.83	Slightly milky	4.5	4.48
2	Brownish red, turbid	4.2	6.69	Brownish red	4.4	6.95
3	Milky	4.1	—	Brownish red	4.3	6.88
4	Milky	4.0	—	Brownish red	4.2	6.68
5	Milky	4.0	—	Milky	4.1	3.84
Standard	—	—	—	—	—	6.89
			Sulfuric acid[6]			
			(Coagulant 0.005–0.004 cc. per 10 cc. latex, while in the case of Hevea the acidity is 0.05–1.0%)			
	(1) With 0.2% solution			(2) With 0.1% solution		
1	Turbid, dark	4.4	4.57	Turbid, dark	4.4	3.94
2	Turbid, dark	4.3	4.54	Turbid, dark	4.4	3.90
3	Milky	4.2	0.97	Turbid, dark	4.3	3.33
4	Milky	4.0	0.15	Turbid, dark	4.3	3.17
5	Milky	—	0.15	Turbid, dark	4.2	4.46
Standard	—	—	—	—	—	4.91
			Nitric acid			
			(Coagulation was best effected with an acidity 0.001–0.004 cc. per 10 cc. latex)			
	(1) With 0.2% solution			(2) With 0.1% solution		
1	Turbid, dark	4.3	3.75	Dark, turbid	4.5	4.38
2	Turbid, dark	4.3	3.76	Dark, turbid	4.5	3.54
3	Milky	4.3	2.35	Dark, turbid	4.5	3.42
4	Milky	4.3	2.72	Dark, turbid	4.5	2.95
5	Milky	4.3	1.54	Dark, turbid	4.5	3.19
Standard	—	—	—	—	—	4.89
			Syrupy phosphoric acid			
			(The range of acidity necessary for coagulation was 0.005–0.01 cc. per 10 cc. latex)			
	(1) With 1% solution			(2) With 0.5% solution		
1	Turbid, dark	4.1	4.18	Turbid, dark	4.3	4.36
2	Milky	<4	2.14	Turbid, dark	4.2	4.43
3	Milky	<4	1.20	Turbid, dark	—	4.30
4	Milky	<4	0.11	Milky	—	0.24
5	Milky	<4	0.07	Milky	—	0.16
Standard	—	—	—	—	—	4.49
			Boric acid			
			(0.005–0.02 g. acid coagulated 10 cc. latex. This coagulant has the advantage of preserving the coagulum)			
	(1) With 0.1% solution			(2) With 0.5% solution		
1	Turbid	4.6	5.49	Brownish red, turbid	4.6	6.89
2	Turbid		6.57	Brownish red, turbid		6.78
3	Milky	to	3.27	Brownish red, turbid	to	6.51
4	Milky		4.67	Brownish red, turbid		6.50
5	Milky	4.4	2.47	Brownish red, turbid	4.4	5.75
Standard	—	—	—	—	—	6.15

Carbonic acid[7]

Air was blown by mouth into latex (10 cc.), whereby a white coagulum and a very slightly turbid serum was obtained. The serum had pH 4.2. The coagulum after usual working weighed 0.2660 gram (2.66%), while the standard weighed 0.2750 gram (2.75%).

TABLE IIB

COAGULATING EFFECT OF ORGANIC ACIDS

Acetic acid[8]

(0.1–0.4 cc. of acid coagulated 200 cc. of latex. Hevea latex requires 0.15–0.6% acidity)

Volume of coagulant (cc.)	Appearance of serum	pH	Percentage D.R.C. on volume basis	Appearance of serum	pH	Percentage D.R.C. on volume basis	Appearance of serum	pH	Percentage D.R.C. on volume basis
	(1) With 1% solution			(2) With 0.5% solution			(3) With 0.25% solution		
1	Brownish red, turbid	4.4	5.46	Turbid	4.5	6.29	Turbid	4.6	6.66
2	Brownish red, turbid	4.3	5.06	Turbid	4.4	4.45	Turbid	4.5	6.64
3	Brownish red, turbid	4.3	5.37	Turbid	4.3	3.06	Turbid	4.4	3.97
4	Brownish red, turbid	4.2	5.04	Turbid	4.2	4.13	Turbid	4.4	4.40
5	Brownish red, turbid	4.1	3.88	Turbid	4.1	3.46	Turbid	4.3	4.50
6	Milky	4.0	0.37	Turbid	—	—	Turbid	—	—
Standard	—	—	—	—	—	—	Turbid	—	6.80

Oxalic acid

	(1) With 10% solution			(2) With 0.5% solution			(3) With 0.25% solution		
1	Dark	4.1	1.74	Dark brown	4.3	2.14	Clear, dark	4.5	2.15
2	Milky	4.0	0.24	Dark brown	4.2	2.15	Clear, dark	4.4	1.55
3	Milky	—	—	Milky	4.0	0.53	Clear, dark	4.4	1.66
4	Milky	—	—	Milky	—	—	Clear, dark	4.1	1.00
5	Milky	—	—	Milky	—	—	—	—	—
Standard	—	—	—	—	—	—	—	—	2.10

TABLE IIC

ACETIC ACID AND ALCOHOL MIXTURE

(1) With constant volume of alcohol				(2) With increased volume of alcohol*				
Volume of coagulant (cc.)				Volume of coagulant (cc.)				
1% acetic acid solution	Alcohol	Appearance of serum	Percentage D.R.C. on volume basis	Percentage acetic acid solution	Alcohol	Appearance of serum	pH	Percentage D.R.C. on volume basis
1	4	Turbid, reddish brown	5.17	1	2	Turbid	4.5	2.30
2	4	Turbid, reddish brown	4.62	2	4	Turbid	4.5	3.12
3	4	Turbid, reddish brown	4.38	3	6	Turbid	4.4	5.56
4	4	Turbid, reddish brown	3.10	3	8	Turbid	4.4	5.92
5	—	—	—	4	10	Turbid	4.4	6.18
standard	—	—	—	Standard	—	—	—	5.98

* The latex mixed with the coagulants was left overnight; dilution with the alcohol gave latter results.

OXALIC ACID, ACETIC ACID AND THEIR MIXTURES WITH ALCOHOL

In a previous communication[9], it was pointed out that acetic acid failed to coagulate latex. That remark was due to the fact that coagulant was not

added with special reference to the hydrogen-ion concentration, and the quantity of acid added exceeded the minimum quantity required to coagulate the latex, hence the latex passed into a second phase in which it became stabilized. Coagulation of the latex of the second stabilized phase has not yet been studied.

TABLE IID

COAGULATION WITH ORGANIC ACIDS

Volume of coagulant (cc.)	Appearance of serum	pH	Percentage D.R.C. on volume basis	Appearance of serum	pH	Percentage D.R.C. on volume basis
	Trichloroacetic acid					
	(0.01022–0.02044 gram was effective in coagulating 10 cc. of latex)					
	(1) With 1% solution			(2) With 0.5% solution		
1	Dark with slimy turbidity	4.3	5.37	Turbid	4.5	3.69
2	Dark with slimy turbidity	4.2	3.78	Turbid	4.4	3.79
3	Dark with slimy turbidity	4.01	1.62	Turbid	4.3	3.59
4	Thick, milky	—	0.53	Turbid	4.3	4.20
5	Thick, milky	—	0.55	Turbid	4.2	3.84
6	Thick, milky	—	0.32	—	—	—
Standard	—	—	—	—	—	4.93
	Formic acid[10]					
	(Increased acidity decreased the percentage of rubber as observed in other cases. A 0.03% solution did not give good results)					
	(1) With 1% solution			(2) With 0.5% solution		
1	Turbid	4.5	7.10	Turbid	4.5	4.00
2	Turbid	—	6.79	Turbid	—	4.24
3	Turbid	—	4.65	Turbid	—	4.48
4	Milky	—	2.66	Milky	—	2.47
5	Milky	—	2.84	—	—	—
Standard	—	—	6.99	—	—	5.00
	Butyric acid					
	(0.001–0.02 gram of acid was found effective to coagulate 10 cc. of latex. Increased acidity stabilized the latex)					
	(1) With 1% solution			(2) With 0.5% solution		
1	Dark and slimy turbidity	4.5	5.42	Dark and slimy turbidity	4.6	5.55
2	Dark and slimy turbidity	4.5	4.91	Dark and slimy turbidity	4.6	4.16
3	Dark and slimy turbidity	4.4	4.59	Dark and slimy turbidity	4.5	3.53
4	Milky	4.3	2.87	Dark and slimy turbidity	4.5	2.44
5	Milky	4.3	2.27	Milky	4.4	1.73
Standard	—	—	—	—	—	4.43
	Tartaric acid					
	(0.01–0.03 gram of acid coagulated 10 cc. of latex)					
	(1) With 1% solution			(2) With 0.5% solution		
1	Dark brown	4.4	2.19	Turbid, dark	4.5	1.75
2	Dark brown	4.2	2.19	Turbid, dark	4.4	1.62
3	Dark brown	4.0	1.98	Turbid, dark	4.2	2.00
4	Milky	—	0.93	Milky	4.0	0.73
5	Milky	—	—	Milky	—	0.72
Standard	—	—	—	—	—	2.00

TABLE IID—*Continued*

Volume of coagulant (cc.)	Appearance of serum	pH	Percentage D.R.C. on volume basis	Appearance of serum	pH	Percentage D.R.C. on volume basis
			Lactic acid			
	(An acidity of 0.005–0.03 brought about coagulation of 10 cc. of latex)					
	(1) With 1% solution			(2) With 0.5% solution		
1	Dark, slimy turbidity	4.4	5.52	Dark, slimy turbidity	4.5	4.22
2	Dark, slimy turbidity	4.2	5.23	Dark, slimy turbidity	4.4	3.32
3	Dark, slimy turbidity	4.0	4.98	Dark, slimy turbidity	4.3	3.44
4	Dark, slimy turbidity	4.0	4.61	Dark, slimy turbidity	4.2	3.93
5	Thick, milky	—	0.96	Dark, slimy turbidity	4.1	4.42
6	Thick, milky	—	1.16	—	—	—
Standard	—	—	—	—	—	5.06
			Citric acid			
	(0.005–0.03 gram of acid coagulated 10 cc. latex)					
	(1) With 1% solution			(2) With 0.5% solution		
1	Turbid, dark	4.4	2.14	Turbid	4.5	2.18
2	Turbid, dark	4.2	2.22	Turbid	4.4	1.87
3	Turbid, dark	4.0	2.00	Turbid	4.2	1.71
4	Turbid, dark	—	1.97	Turbid	4.0	1.71
5	Turbid, dark	—	1.75	Turbid	—	1.53
6	Turbid, dark	—	1.15	—	—	—
Standard	—	—	—	—	—	2.10

Stabilization of Latex or its Passage to the Second Phase[11].—If acid is added to the latex so as to drop the pH value to 4.0, the latex remains milky, does not coagulate, and passes into the second phase or zone (*cf.* Hevea). Latex (100 cc.) was mixed with 0.5 cc. of hydrochloric, nitric and sulfuric acids in separate corked bottles. On keeping for three months no coagulation occurred. Cream particles floated to the surface of the serum, but they redispersed on shaking.

COAGULATION WITH ALKALIES AND ORGANIC BASES

Alkalies.—In every case, experiments were done with alkalies. The solution of the alkali was added dropwise to the latex, with stirring and slight warming, till a white coagulum separated from a yellow or reddish brown serum.

Organic Bases.—The base was added to 10 cc. of latex, whereby coagula were obtained which emitted an odor of the base and had brown streaks. The coagula were washed with water and finally with alcohol, but still the smell of the base persisted. Due to the immiscibility of the bases with water, smaller quantities of the bases were not used excepting pyridine.

COAGULATION BY SALTS

Very dilute solutions of salts were used, because latex is coagulated by tap water containing only small quantities of dissolved substances. The hydrogen-ion concentration values were helpful as a guide to the coagulation point when

TABLE III

COAGULATING EFFECT OF ALKALI AND ORGANIC BASES

Volume of coagulant (cc.)	Appearance of serum	pH	Percentage D.R.C. on volume basis	Volume of coagulant (cc.)	Appearance of serum	pH	Percentage D.R.C. on volume basis
			Lime water				
	(For pH values from 6.2 to 7.4 bromothymol blue and for 8.9 universal indicator were used)						
	(1) With saturated lime water diluted in the ratio 10 : 19 (lime water : tap water)				(2) With saturated lime water diluted in the ratio 1 : 1 (lime water : tap water)		
10	Milky	4.6	—	10	Milky	5.2	2.23
20	Milky	4.8	—	20	Milky	6.2	2.40
30	Milky	5.0	3.04	30	—	—	—
Standard	—	—	3.89	Standard	—	—	2.90
	(3) With saturated lime water at 31° (N/25.5 approximately)				(4) Coagulant after mixing and warming gave a precipitate*		
10	Dirty	7.1	2.50	10	Pinkish, dirty	—	1.85
20	Clear red	7.2	3.70	20	Clear red	7.4	3.26
30	—	—	—	30	Clear red	8.4	3.69
Standard	—	—	—	Standard	—	—	3.89

* The percentage of the coagulum was reduced owing to the decrease in alkalinity.

			Potassium hydroxide				
	(Bromothymol blue was used as indicator)						
	(1) With 0.05 N solution				(2) With 0.05 N solution		
10	Dirty light pink	7.2	1.69	20	Clear red	7.7	3.50
Standard	—	—	2.90	30	Clear red	—	3.30
				Standard	—	—	3.89
			Sodium carbonate				
	(Bromothymol blue was used as an indicator)						
	(1) With 0.05 N solution				(2) With 0.05 N solution		
10	Dirty pink	6.5	1.69	30	Clear red	7.7	3.65
20	Dirty pink	7.5	1.80	Standard	—	—	3.89
Standard	—	—	2.90				
			Sodium hydroxide[12]				
10 of 0.05 N solution	Dirty pink	7.2	—	1 of N solution	Clear red	7.7	3.55
20 of 0.05 N solution	Clear red	7.7	3.40	2.5 of N solution	No coagulation, no separation of coagulation and serum on adding 2.5 cc. more		
20 of 0.1 N solution	Clear red	7.7	3.67				

Slight variations in D.R.C. percentages are due to variation sampling.

Ammonium hydroxide

This is used for the preservation of Hevea latex. When added to the latex of *Cryptostegia* a big spongy clot of rubber separated, which either turned black or developed black streaks on its upper surface; this observation indicated that ammonia also could be used as a coagulant.

	(1) With 0.1% solution (0.1 cc. of ammonia, in 100 cc. water, d = 0.88)				(2) With 0.05% solution		
1	Turbid	—	4.98	1	Turbid	—	4.41
2	Turbid	—	5.81	2	Turbid	—	2.68*
3	Turbid	—	3.10	3	Turbid	—	5.72
4	Turbid	—	5.36	Standard	Turbid	—	5.54

* The variations in the percentage of the coagula are probably due to the escape of ammonia from the mixture on warming and keeping.

TABLE III—*Continued*

Volume of coagulant (cc.)	Appearance of serum	pH	Percentage D.R.C. on volume basis	Volume of coagulant (cc.)	Appearance of serum	pH	Percentage D.R.C. on volume basis
			Quinoline				
	(1 cc. weighed 1.032 g. The coagula had brown streaks)						
0.2	Slightly turbid	—	7.6*	1.4	Slightly turbid	—	7.25
0.4	Slightly turbid	—	7.60	1.6	Slightly turbid	—	7.06
0.8	Slightly turbid	—	7.61	2.5	Slightly turbid	—	7.25
1.2	Slightly turbid	—	7.60	Standard	Slightly turbid	—	6.56

* Variations may be due to washing and increased amount of the base which had no advantage.

			Aniline[13]				
	(1 cc. weighed 1.021 g. The coagula were slightly colored)						
0.2	Slightly turbid	—	6.90	1.4	Slightly turbid	—	6.67
0.6	Slightly turbid	—	7.05	1.8	Slightly turbid	—	6.65
1.2	Slightly turbid	—	6.00	Standard	—	—	6.56

Aniline hydrochloride

The solution was prepared by dissolving 0.5 gram in 100 cc. tap water. A small volume of 0.5% solution gave a coagulum, but in most cases the serum remained milky. As this salt did not yield good results, salts of other cases were not used[14].

1	Turbid	—	5.69	4	Milky	—	Nil*
3	Turbid	—	5.54	Standard	—	—	6.56

* Eleven experiments were done with increased quantity of the coagulant, but none gave any coagulum after Experiment 3.

			Toluidine				
0.2	Slightly turbid	—	7.07	1.4	Slightly turbid	—	6.88
0.4	Slightly turbid	—	7.36	1.6	Slightly turbid	—	6.44
0.8	Slightly turbid	—	6.98	2.5	Slightly turbid	—	6.67
1.2	Slightly turbid	—	7.18	Standard	—	—	6.55

Pyridine

One cc. weighed 1.0206 gram. The coagula obtained from the bases (quinoline, aniline, toluidine and pyridine) were very spongy and the texture was weak and had very little tensile strength compared to the coagula obtained from acid coagulation. The experiments were performed by adding free base to the latex as well as by adding its water solution. The coagula emitted a pyridine smell and were white.

	(1) With 1% solution				(2) With 0.5% solution		
0.2	Brownish red, turbid	—	6.52	1	Turbid	4.6	5.30
0.6	Brownish red, turbid	—	6.60	3	Turbid	4.9	5.28
1.0	Brownish red, turbid	—	6.46	5	Turbid	5.0	4.95
1.4	Brownish red, turbid	—	6.70	9	Turbid	5.3	4.89
2.0	Brownish red, turbid	—	6.86	10	Turbid	5.4	5.24
Standard	—	—	6.56	Standard	—	—	4.89

water, acids and alkalies were used as coagulants, but they led to no definite information with most of the solutions of the salts used for coagulating the latex. Extremely weak solutions of sodium and calcium chlorides, aluminum and ammonium sulfate, and alum gave good results. In all these experiments, 0.1 and 0.05 per cent solutions of the salts were used.

TABLE IV

COAGULATING EFFECTS OF VARIOUS SALTS

Volume of coagulant (cc.)	Appearance of serum	pH	Percentage D.R.C. on volume basis	Appearance of serum	pH	Percentage D.R.C. on volume basis
			Alum[15]			
	(1) With 0.05% solution			(2) With 0.05% solution		
1	Turbid	4.6	6.82	Turbid	4.6	7.30
2	Turbid		7.13	Turbid		6.75
3	Milky	to	4.89	Turbid	to	6.85
4	Milky		5.09	Turbid		6.51
5	Milky	4.7	5.79	Turbid	4.5	6.21
Standard	—	—	—	—	—	7.00
			Aluminum sulfate			
	(1) With 0.1% solution			(2) With 0.05% solution		
1	Turbid	4.6	5.78	Turbid	4.6	6.90
2	Turbid		4.12	Turbid		7.30
3	Turbid	to	3.40	Turbid	to	6.38
4	Turbid		3.90	Turbid		6.25
5	Turbid	4.5	3.40	Turbid	4.5	6.31
Standard	—	—	—	—	—	7.00
			Calcium chloride[16]			
	(1) With 0.1% solution			(2) With 0.05% solution		
1	Turbid	4.6	7.60	Turbid	4.6	8.09*
2	Turbid		6.08	Turbid		7.16
3	Turbid		6.10	Turbid	to	6.86
4	Turbid	to	5.09	Turbid	4.5	6.41
5	Turbid		6.18	Turbid	—	—
6	Turbid	4.5	5.40	Turbid	—	—
Standard	—	—	—	—	—	6.89
			Sodium chloride			
	(1) With 0.1% solution			(2) With 0.05% solution		
1	Milky	4.5	3.79	Turbid	4.5	7.15
2	Turbid	4.5	6.32	Turbid	4.5	6.68
3	Turbid	4.5	6.03	Turbid	4.5	5.97
4	Turbid	4.5	5.94	Turbid	4.5	6.18
5	Turbid	4.5	6.10	—	—	—
Standard	—	—	—	—	—	—
			Ammonium sulfate			
	(1) With 0.1% solution			(2) With 0.05% solution		
1	Turbid	4.5	6.40	Turbid	4.5	6.21
2	Turbid	4.5	6.24	Turbid	4.5	5.78
3	Turbid	4.5	5.16	Turbid	4.5	6.40
4	Turbid	4.5	5.99	Turbid	4.5	5.80
5	Turbid	4.5	5.71	Turbid	4.5	6.01
Standard	—	—	—	—	—	6.89

* Variations due to sampling. Sometimes cream comes on the top and, if not properly shaken, causes fluctuations in D.R.C.

TABLE IV—*Continued*

Volume of coagulant (cc.)	Appearance of serum	pH	Percentage D.R.C. on volume basis	Appearance of serum	pH	Percentage D.R.C. on volume basis
			Aluminum chloride			
	(1) With 0.1% solution			(2) With 0.05% solution		
1	Turbid	4.4	6.08	Milky	4.5	3.51
2	Turbid		4.74	Milky	4.5	3.52
3	Turbid		3.98	Turbid	4.5	5.53
4	Turbid	to	4.04	Turbid	4.5	5.07
5	Milky		1.50	Turbid	4.5	4.84
6	Milky	4.3	2.71	—	—	—
Standard	—	—	—	—	—	6.89
			Mercuric chloride[17]			
	(1) With 0.1% solution			(2) With 0.05% solution		
1	Turbid	4.5	6.19	Thick, milky	4.5	3.96
2	Thick, milky	4.5	2.38	Thick, milky	4.5	2.80
3	Thick, milky	4.5	1.25	Thick, milky	4.5	1.52
4	Thick, milky	4.5	1.13	Thick, milky	4.5	1.92
5	Thick, milky	4.5	0.88	—	—	—
Standard	—	—	—	—	—	6.89
			Nickel sulfate			
	(1) With 0.1% solution			(2) With 0.05% solution		
1	Turbid	4.5	5.94	Turbid	4.5	4.65
2	Turbid	4.5	5.65	Turbid	4.5	5.67
3	Turbid	4.5	5.38	Milky	4.5	3.23
4	Turbid	4.5	4.20	Milky	4.5	1.70
5	Milky	4.5	3.00	—	—	—
Standard	—	—	—	—	—	6.89
			Cobalt nitrate			
	(1) With 0.1% solution			(2) With 0.05% solution		
1	Milky	4.5	3.78	Milky	4.5	3.05
2	Milky		3.10	Milky		3.90
3	Milky	to	3.84	Milky	to	4.25
4	Milky		2.99	Milky		4.88
5	Milky		3.83	Milky	4.4	3.37
6	Milky	4.4	3.03	—	—	—
Standard	—	—	—	—	—	6.89
			Lead acetate			
	(1) With 0.1% solution			(2) With 0.05% solution		
1	Turbid	4.5	4.28	Turbid	4.5	5.14
2	Milky		3.50	Milky	4.5	3.55
3	Milky		3.94	Milky	4.5	4.70
4	Milky	to	3.96	Milky	4.5	2.26
5	Milky		2.94	Milky	4.5	3.06
6	Milky	4.3	3.52	Milky	4.5	—
Standard	—	—	—	—	—	6.89

TABLE IV—*Continued*

Volume of coagulant (cc.)	Appearance of serum	pH	Percentage D.R.C. on volume basis	Appearance of serum	pH	Percentage D.R.C. on volume basis
			Copper sulfate			
			(Coagulum was brownish)			
	(1) With 0.1% solution			(2) With 0.05% solution		
1	Turbid	4.4	6.40	Turbid	4.4	5.58
2	Turbid		6.41	Turbid		5.63
3	Turbid	to	5.05	Turbid	to	5.86
4	Turbid		4.59	Turbid		5.58
5	Turbid		2.03	Turbid	4.3	3.49
6	Turbid	4.3	3.59	—	—	—
Standard	—	—	—	—	—	6.89
			Zinc chloride			
	(1) With 0.1% solution			(2) With 0.05% solution		
1	Milky	4.5	4.72	Milky	4.5	3.91
2	Milky	4.5	3.63	Milky	4.5	5.82
3	Milky	4.5	2.32	Milky	4.5	2.52
4	Milky	4.5	3.35	Milky	4.5	2.67
5	Milky	4.5	2.71	Milky	4.5	3.70
6	Milky	4.5	2.97	—	—	—
Standard	—	—	—	—	—	6.38
			Manganese sulfate			
	(1) With 0.1% solution			(2) With 0.05% solution		
1	Turbid	4.5	7.53	Turbid	4.5	7.37
2	Turbid	4.5	5.52	Turbid	4.5	7.41
3	Turbid	4.5	4.95	Turbid	4.5	7.03
4	Turbid	4.5	5.01	Turbid	4.5	6.78
5	Turbid	4.5	4.99	Turbid	4.5	6.86
6	Milky	4.5	3.52	—	—	—
Standard	—	—	—	—	—	7.89
			Potassium ferrocyanide			
	(1) With 0.1% solution			(2) With 0.05% solution		
1	Slightly turbid	4.5	7.12	Turbid	4.5	5.62
2	Slightly turbid	4.5	7.22	Turbid	4.5	5.76
3	Milky	4.5	1.80	Turbid	4.5	6.05
4	Milky	4.5	1.44	Turbid	4.5	5.71
5	Milky	4.5	1.98	Turbid	4.5	5.22
Standard	—	—	—	—	—	7.89
			Potassium ferricyanide			
	(1) With 0.1% solution			(2) With 0.05% solution		
1	Turbid	4.5	7.35	Turbid	4.5	8.21
2	Turbid	4.5	7.13	Turbid	4.5	7.01
3	Turbid	4.5	4.53	Turbid	4.5	6.12
4	Milky	4.5	3.56	Turbid	4.5	7.38
5	Milky	4.5	3.76	Turbid	4.5	5.21
Standard	—	—	—	—	—	7.89

TABLE IV—*Continued*

Volume of coagulant (cc.)	Appearance of serum	pH	Percentage D.R.C. on volume basis	Appearance of serum	pH	Percentage D.R.C. on volume basis
			Sodium fluosilicate			
	(1) With 0.1% solution			(2) With 0.05% solution		
1	Milky	—	4.80	Turbid	—	5.87†
2	Milky	—	2.30	Milky	—	2.73
3	Milky	—	1.50	Milky	—	3.21
4	Milky	—	2.55	Milky	—	2.11
5	Milky	—	1.97	Milky	—	3.61
Standard	—	—	1.92	—	—	7.89

† It appears that still lesser quantities of the coagulant will give better results.

TABLE V

COAGULATING EFFECT OF PROTEIN PRECIPITATING AND MISCELLANEOUS REAGENTS

Volume of coagulant (cc.)	Appearance of serum	pH	Percentage D.R.C. on volume basis	Appearance of serum	pH	Percentage D.R.C. on volume basis
			Picric acid			
	(1) With 1% solution			(2) With 0.5% solution		
1	Clear yellow	4.4	2.17	Clear yellow	4.5	2.17
2	Turbid yellow	4.2	1.70	Clear yellow	4.4	3.00
3	Deep yellow flocculation	4.2	—	Yellow flocculation	4.4	1.62
4	Deep yellow flocculation	4.0	—	Yellow flocculation	4.3	0.37
5	Deep yellow flocculation	—	—	Yellow flocculation	4.3	—
Standard	—	—	2.00	—	—	4.49
			Tannic acid[20]			
	(1) With 1% solution			(2) With 0.5% solution		
1	Dark violet, turbid	4.5	2.26	Dark violet, turbid	4.5	1.96
2	Dark violet, turbid		2.05	Dark violet, turbid		2.10
3	Dark violet, turbid	to	1.89	Dark violet, turbid	to	1.82
4	Dark violet flocculation		0.43	Dark violet, turbid		1.12
5	Dark violet flocculation	4.3	0.68	Dark violet, turbid	4.4	1.05
Standard	—	—	—	—	—	2.00*

* Latex was received at different intervals of time and hence the fluctuations in D.R.C.

			Phosphotungstic acid			
	(1) With 1% solution			(2) With 0.5% solution		
1	Flocculation	4.6	0.06	Dark turbid	4.6	2.27
2	Flocculation	4.5	0.21	Dark turbid	—	2.24
3	Turbid	4.4	2.25	Dark turbid	—	1.32
4	Turbid	4.3	3.00	Dark turbid	—	1.89
5	Turbid	4.3	3.47	Dark turbid	—	2.20
Standard	—	—	—	—	—	4.49

To latex (10 cc.) was added, with stirring, 40 per cent formalin in portions of 0.1 cc. A small pellet of rubber formed when 0.5 cc. of the solution was added. Complete coagulation did not take place even after adding 1 cc., but the latex thickened. On diluting the mixture with 50 cc. of water, flocculation occurred and the flocks formed the surface layer, leaving below a clear layer of serum. On stirring, the flocks redistributed but did not coalesce nor stick together after collection on a filter bed. The filtered mass was washed and dried in an air oven at 90–95° and weighed 0.5300 gram (5.30%). There was no change in the hydrogen-ion concentration of the serum before dilution. When this experiment failed, lesser concentrations were used, and the results show that very dilute solutions of formaldehyde can bring about coagulation.

TABLE V—*Continued*

Volume of coagulant (cc.)	Appearance of serum	pH	Percentage D.R.C. on volume basis	Appearance of serum	pH	Percentage D.R.C. on volume basis
			Formaldehyde			
	(1) With 0.1% solution			(2) With 0.05% solution		
1	Brownish, turbid	—	7.03	Brownish, turbid	—	6.80
2	Brownish, turbid	—	6.36	Brownish, turbid	—	7.12
3	Milky, turbid	—	2.73	Brownish, turbid	—	6.64
4	Milky, turbid	—	1.12	Brownish, turbid	—	6.02
5	Milky, turbid	—	1.32	Brownish, turbid	—	1.58
Standard	—	—	—	—	—	6.89
			Serum			
	Serum was added to latex and the mixture was kept in boiling water for 15 minutes, but no change occurred in the pH value. The results show that an increase in the volume of serum decreased the percentage of coagulum and accordingly lesser quantities of serum were used and gave better results.					
5	Milky	4.6	5.02	2.5	Turbid	— 6.69
10	Milky	4.6	3.74	3.0	Turbid	— 5.89
20	Milky	4.6	0.10	3.5	Turbid	— 6.36
0.5	Turbid	—	6.89	4.0	Turbid	— 5.78
1.0	Turbid	—	6.85	4.5	Turbid	— 6.06
1.5	Turbid	—	7.21	5.0	Turbid	— 6.60
2.0	Turbid	—	7.27	5.5	Turbid	— 5.43
				Standard	—	— 6.89

Coagulation and Hydration.—Alcohol was used under this head and the details are given under reagents used for coagulating proteins.

Coagulation and Dehydration.—Anhydrous potassium carbonate, anhydrous sodium sulfate, sodium and potassium hydroxides, phosphorus pentoxide and zinc chloride were used. In every case 1 gram of the reagent was added to 10 cc. of latex. Good white coagula were obtained with anhydrous sodium sulfate and zinc chloride; a colored coagulum was obtained with potassium carbonate. With potassium and sodium hydroxides pasty masses were formed. Phosphorus pentoxide thickened the latex.

Protein Coagulating Reagents. Alcohol[18].—Ninety-eight per cent alcohol was added dropwise to latex (20 cc.). On adding 11 cc., a white coagulum and a turbid brownish red serum were obtained. The coagulum after sheeting weighed 1.2430 grams or 6.22 per cent. The turbidity of the serum persisted, even after adding a further volume of 13 cc. of alcohol, and appeared to be due to the coagulated and separated proteins, etc. The pH of the serum remained unchanged (4.6). Thus the volume of alcohol required to coagulate latex is one-half the volume of latex.

Acetone.—Acetone was added dropwise from a burette to latex (10 cc.). On adding 10 cc., a white coagulum and a brownish red serum were obtained. The pH value remained unchanged[19].

Besides alcohol and acetone, picric, tannic, phosphotungstic acids were used for coagulating latex. The quantities of coagulants required to coagulate 10 cc. of latex were 0.05–0.1; 0.05–0.2; and 0.025–0.05 gram, respectively. The coagulum from picric acid was yellow and from tannic acid violet, but it was white from phosphotungstic acid.

Lemon Juice[21].—Latex (50 cc.) was mixed with lemon juice (2 cc.). On keeping for 24 hours it thickened, but a coagulum did not separate. How-

ever, on slight warming coagulation took place, and the pH value decreased from 5.0 to 4.5. The serum coagulated two further quantities of the latex.

Curd[22].—Sour curd was strained through muslin and 1 cc. of this was added to latex (50 cc.). The mixture thickened on keeping overnight and, on stirring and gentle warming on the water-bath a coagulum and serum separated. The pH dropped from 5.0 to 4.7. The serum coagulated two fresh quantities of latex.

Molasses.—Thick molasses (2 cc.) was added to latex (50 cc.). On keeping overnight no change occurred in the consistency of the mixture, but after stirring and warming on the water-bath for 15 minutes, a coagulum separated, and the pH value dropped from 5.0 to 4.5.

COAGULATION BY ADDITION OF WATER

Water was added dropwise to latex (50 cc.) and on addition of 20 volumes of water (1,000 cc.) flocculation took place and the particles coalesced to form a jellylike spongy mass, leaving behind a clear straw-colored serum. The gelatinous mass on squeezing, pressing and washing formed a membrane which turned transparent on dehydration at 100°. The pH values for distilled water, latex and serum were 7.0, 5.0 and 6.2, respectively. Latex of *C. grandiflora* can be coagulated with distilled water[23].

The same behavior was observed with tap water; 12 to 16 volumes were necessary for complete coagulation and pH values for tap water, latex and serum were 7.5, 5.0 and 7.5, respectively. But when latex was diluted with water and warmed to 80–90°, the dilution was reduced to 8–10 volumes. When latex was added to boiling water, the volume was further reduced to 6, and D.R.C. percentages of 3.8 and 3.5 were obtained when latex (10 cc) was coagulated with tap water (200 and 60 cc., respectively), 5 volumes brought about partial coagulation, while 4 volumes of water produced flocculation, and the flocks did not agglomerate, even on keeping in boiling water, but stuck together when collected on a filter and washed.

When fresh and saline waters from the Estate (Imperial Agricultural Research Institute Area) and river and canal waters were used, similar results were obtained. It may be pointed out that salinity decreased the extent of dilution, while cold and ice-cold water was of no advantage.

In the light of results of laboratory experience, the water coagulation method was developed and submitted to semilarge scale trials. A quantity of latex (6.5 lbs.) was diluted with hot water ten times. The latex set to a spongy mass which formed a sheet $6\frac{1}{2} \times 4\frac{1}{4} \times 7\frac{1}{6}$ inches, weighing $5\frac{1}{4}$ ounces.

Formation of a Black Substance on Coagulation with Water.—When latex was coagulated with water and the coagulum and serum were allowed to stand overnight, a black substance was formed over the coagulum as well as the serum. The liquid obtained by pressing the coagulum was also rich in it.[24] The black substance once developed on the coagulum was not removed on washing with water or acidulated water. Investigations of the cause of this revealed that alkalinity helps the formation of this black substance and acidity retards it[25] When after sheeting and washing, the coagulum was dipped for 15 minutes in 0.05% solution (acid 0.05 cc. in tap water 100 cc.) of hydrochloric, sulfuric and nitric acids, it remained white and could be kept under water exposed to the air without change of color. The best results were obtained with nitric acid. The water should be changed from day to day, otherwise it develops a foul smell and bacteria. When a sheet of rubber was kept immersed in water for two months after this treatment, it remained white.

When the sheet was partially immersed in water, the portion exposed to the air became violet, brown, and finally deep in color.

AUTOCOAGULATION

When latex is allowed to stand for a few days at room temperature (28–30°), autocoagulation results with the separation of a white spongy clot of rubber and a clear reddish brown serum having pH value 4.2. In a previous communication[26] the pH was recorded as 4.6. The difference in acidity due to seasonal variations may be responsible for this. The coagulum when pressed into sheets had good tensile strength and elasticity and did not show any tendency to deteriorate or decompose. This autocoagulation appeared to be due to the changes from decomposition by enzymes, etc., in the latex. An increase in the acidity and a shift of pH value from 4.6 to 4.2 further confirmed this observation. In some cases when the latex was allowed to stand quietly in uncorked bottles, the surface of latex turned violet-brown and finally black and yellowish moulds developed on it. The same moulds developed in the serum when it was exposed to air, and were identified as (1) *Aspergillus flavus ovyzae* and (2) *Aspergillus niger van Teighen*. A sheet of undried rubber when kept in water without changing it and exposed to the air developed a foul smell, and the examination showed bacteria[27] and spores of saprophytic fungus like *Cladosperring Sp.*, etc. Thus the change in autocoagulation can be attributed to the action of enzymes, microörganisms and also to some other unknown causes[28].

Autocreaming.—When the latex was allowed to stand for a day or two, its cream or suspended particles floated to the surface, leaving below a clear serum which could be syphoned off. The cream formed a big clot of a spongy mass on dilution or washing with water. The cream also stuck by the agglomeration of particles when collected on a filter. This method is of practical importance, and can be recommended for the coagulation of rubber. It has the advantage that it requires less dilution for the coalescence of the rubber particles and also eliminates big coagulating equipment[29]. The only necessary thing is to find a preservative so that it will not develop any bad smell due to decomposition on keeping, or when transported from place to place. This work will form part of a separate communication.

COAGULATION BY HEAT

Natural Heat.—When a twig is cut, the latex at the cut end dries up and forms a seal which can be pulled, and the latex that flows down coagulates on the ground. Similarly when the whip is scratched by a knife or a needle the small drops of latex ooze out and dry on it in small globules. These are examples of coagulation due to natural heat.

(2) *Artificial Heat. Dry Heat.*—When latex (10 cc.) was warmed on a sand or water-bath, it began to form a thin film or membrane on the upper surface of the latex at about 50°, then thickened, gradual and complete coagulation took place at about 80–84°, and a little brown serum[30] was left. The pH value of the latex remained unchanged (4.6). This process is important when whole rubber is required.

Smoking.—When latex is exposed to the action of smoke it becomes concentrated and impregnated with smoke acids, creosote oil, etc. This impregnation of the latex causes its coagulation[31]. A smoking chamber designed in

this laboratory is shown in Figure 1. It consists of a fire place and an upper chamber provided with a chimney and an arrangement for hanging rubber sheets. At the bottom the chamber is connected with the fire place by a perforated disc through which the smoke enters from the fire place to the upper chamber. The paddy husk was used in the fire place for producing smoke. Rubber sheets dried in this smoking chamber suffered a loss of 31

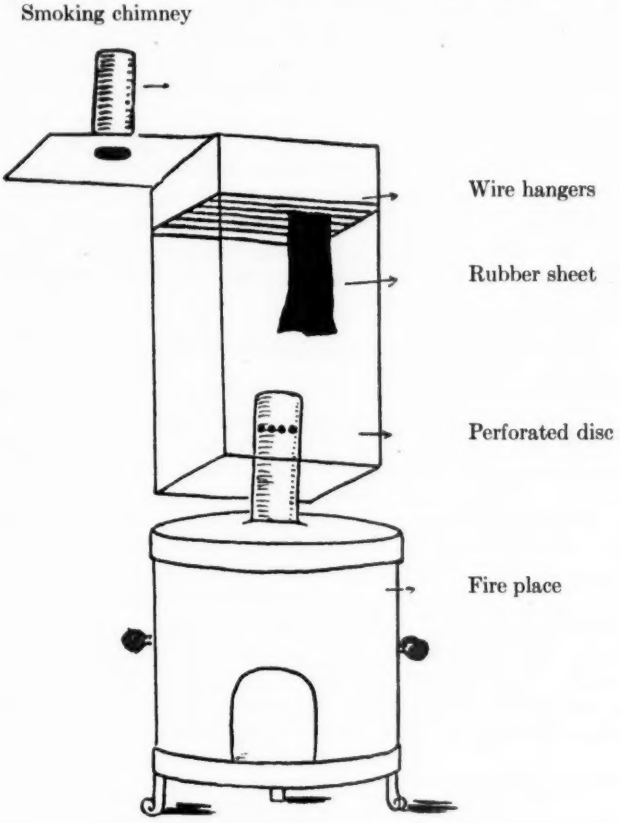

FIG. 1

and 17 per cent on drying for three hours. The lesser moisture content in the second sheet may be due to good pressing. The sheet after drying resembled cured rubber, and a strip cut from the sheet could be pulled four to five times its size and had a very good tensile strength and elasticity.

Moist Heat or Steam.—Steam was passed in a beaker containing latex (20 cc.) for three minutes till the volume increased to 30 cc., whereby a white coagulum and a turbid serum were obtained. The experiment was repeated three times. The coagula after washing and drying at 90–95° gave 6.61, 5.90, 6.0 per cent.

COAGULATION BY CENTRIFUGING AND MECHANICAL SHAKING

Shaking.—Latex (10 cc.) was shaken in a corked test-tube till it separated into a coagulum and a clear straw-colored serum. The pH value of the latex

remained unchanged. The D.R.C. amounted to 2.47 per cent, which is comparable to the percentage obtained by coagulating an equal volume of latex with water.

Centrifuging.—Latex (10 cc.) was centrifuged in a rapidly rotating centrifuge. A coagulum separated as a hard disc or button and came to the top within ten minutes. (The percentages of D.R.C. from 4 observations were 5.5, 6.2, 6.3, and 6.6, respectively.) The serum was turbid, and on dilution with water yielded a further quantity of coagulum. (The D.R.C. of 4 observations were 1.0, 0.6, 0.5 and 0.2 per cent.) The pH of the latex remained unchanged. This process can be used for the coagulation of latex on a large scale[32].

Separation of Coagulum from the Latex by Alpha-Alpha Separator.—A liter of latex was churned, whereby a clear serum was obtained on feeding the latex a number of times. The coagulum stuck to the internal spherical balls and clogged the machine. The whole operation of the separation of coagulum was completed in ten minutes. This is also suggestive of the fact that a centrifuge used for sugar could be used for the separation of rubber from the latex on a large scale.

COAGULATION BY ELECTRIC CURRENT

A current was passed through latex diluted with water by using copper electrodes. Flocculation occurred, but a clear serum was not obtained. The whole mass became dirty yellow and on keeping finally turned black. With carbon electrodes neither the serum nor the coagulum turned black on passage of the current. Finally the current was passed in a U-tube with platinum electrodes, whereby the dispersed particles began to move towards the anode and bubbles began to come out copiously at the cathode at which there was also deposition of a substance which first turned yellow and finally brown and black. The deposited matter at the anode, even after keeping for a week, remained white and came to the top in the limb of the U-tube leaving the clear serum below. The experiment indicates that the charge carried by the dispersed particles of the latex is negative. The pH value of the serum was 3.8, and so the change is a chemical one brought about by the changes of decomposition which resulted in increased acidity of the serum[33].

Stages of Coagulation[34].

(1) *Formation and Separation of Cream.*—Latex was allowed to stand quietly at room temperature (25–31°) and was then diluted with water (4 volumes). Fine suspended particles of latex slowly separated out and began to float to the surface. When the liquid was stirred the particles again mixed with the serum and became redistributed uniformly so that latex was again formed.

(2) *Separation of Latex into Cream and Clear Serum.*—The fine white particles of cream in (1) further agglomerated, formed bigger particles of cream, and collected on the surface, forming an upper surface of cream and lower layer of clear serum. The cream was redistributed and separated by filtration.

(3) *Coagulation.*—The upper white cream on touching with a glass rod formed a voluminous spongy and jellylike mass, due to the formation of a network of rubber threads and fibres by their crossings and recrossings, and the whole clot could be lifted bodily from the serum. At this stage, when the fine fibres or threads of rubber united, they were no longer particles of cream

which could be redistributed in the serum on shaking or stirring. The cause has not been examined, but probably the change is brought about by the disruption of electrical and molecular cohesive forces.

CONFIRMATION OF THE RESULTS OF COAGULATION ON A SEMILARGE SCALE

The following coagulants were used to coagulate 1 pound of latex of *C. grandiflora* to confirm the results obtained by coagulating 10 cc. of the latex. The following observations confirm the previous findings.

TABLE VI

PERCENTAGES OF D.R.C. FROM 1 POUND OF LATEX

No.	Name of the coagulant	Amount of the coagulant	Volume of water in which the coagulant was dissolved (cc.)	Weight of D.R.C. (grams)	Percentage D.R.C. on weight basis
1	Hydrochloric acid	0.1075 cc.	43	24.69	5.74
2	Nitric acid	0.043 cc.	43	23.76	5.54
3	Acetic acid	0.43 cc.	43	26.93	6.26
4	Sulfuric acid	0.172 cc.	43	28.59	6.65
5	Sodium hydroxide	0.43 g.	43	28.38	6.60
6	Ammonia (concd.)	0.86 cc.	—	23.05	5.36
7	Pyridine	0.516 cc.	50	28.19	6.56

Cost of Coagulation.—Table VII shows the number of pounds of latex which can be coagulated by one pound of the coagulant.

TABLE VII

Name of coagulant	Pounds of latex coagulated by 1 pound of coagulant
Hydrochloric acid	3,800
Sulfuric acid	1,500
Nitric acid	9,250
Sodium hydroxide	269
Boric acid	21,500
Oxalic acid	2,150
Citric acid	2,150
Calcium chloride	21,500
Sodium chloride	21,500
Ammonium sulfate	21,500
Aluminum sulfate	21,500
Alum	21,500
Acetic acid	200
Formic acid	300

CONCLUSIONS

1. Coagulation can be brought about by methods which are physical and chemical in nature. The chemical methods are suitable for the coagulation of latex on a large scale.

2. The latex coagulates at a pH range of 4.2–7.5.

3. The range toward pH 4.2 is reached by acids and acid salts.

4. Coagulation when effected by chemical reagents, by autocoagulation or by passage of an electric current is always accompanied by a change in the hydrogen-ion concentration of the latex.

5. Dilute solutions of alkalies, acids and of some salts give very good results.

TABLE VIII

COAGULATING EFFECT OF VARIOUS SUBSTANCES††

Quantities of coagulants in grams or cc. and water of dilution per liter of 2.7 per cent *Cryptostegia grandiflora* latex

Name of coagulant	Coagulant in g. or cc. per liter		Volume of water* in which the coagulant was dissolved	
	Minimum	Maximum	Minimum (cc.)	Maximum (cc.)
1. Hydrochloric acid	0.25 cc.	1.0 cc.	100	400
2. Hydrobromic acid	0.50	3.0	100	600
3. Hydriodic acid	0.50	3.0	100	600
4. Hydrofluoric acid	0.50	2.0	100	400
5. Sulfuric acid	0.40	0.5	100	200
6. Nitric acid	0.10	0.2	100	200
7. Phosphoric acid (syrupy)	0.5	1.0	100	200
8. Boric acid	0.05 g.	0.3 g.	100	600
9. Acetic acid	0.25 cc.	4.0 cc.	100	400
10. Trichloroacetic acid	0.5 g.	2.0 g.	100	400
11. Formic acid	0.25 cc.	2.0 cc.	100	400
12. Butyric acid	0.5	3.0	100	600
13. Tartaric acid	0.5 g.	1.2 g.	100	400
14. Lactic acid	1.0 cc.	3.0 cc.	100	600
15. Oxalic acid	0.5 g.	1.2 g.	100	300
16. Citric acid	0.5	2.0	100	400
17. Lime water	10000 cc. of $N/25.5$ solution		—	—
18. Potassium hydroxide‡	5.6 g.	5.6 g.	—	—
19. Sodium carbonate‡	11.0	11.0	—	—
20. Sodium hydroxide‡	4.0	4.0	—	—
21. Quinoline†	20 cc.	—	—	—
22. Aniline†	20.0	—	—	—
23. Toluidine†	20.0	—	—	—
24. Pyridine	0.5	2.0	100	400
25. Alum	0.05 g.	0.25	100	500
26. Aluminum sulfate	0.05	0.25	100	500
27. Calcium chloride	0.05	0.25	100	500
28. Sodium chloride	0.05	0.20	100	400
29. Ammonium sulfate	0.05	0.25	100	500
30. Aluminum chloride**	0.1	0.1	100	—
31. Mercuric chloride**	0.1	0.1	100	—
32. Nickel sulfate**	0.1	0.1	100	—
33. Cobalt nitrate**	0.2	0.2	200	—
34. Lead acetate	0.05	0.05	100	—
35. Copper sulfate	0.05	0.20	100	—
36. Zinc chloride**	0.1	0.1	100	—
37. Manganese sulfate	0.05	0.25	100	500
38. Potassium ferrocyanide	0.05	0.15	100	300
39. Potassium ferricyanide	0.05	0.20	100	400
40. Sodium fluosilicate	0.05	0.05	100	—
41. Picric acid**	1.0	1.0	100	—
42. Tannic acid**	1.0	1.0	100	—
43. Lemon juice	40.0 cc.	40.0 cc.	—	—
44. Curd	20.0	20.0	—	—
45. Water	6000	12000	—	—
46. Formalin	0.05	0.2	100	400
47. Alcohol (98%)	555.0	555.0	—	—
48. Acetone	1000.0	1000	—	—

* No definite rule can be fixed for the minimum and maximum dilution. A concentrated solution would require less dilution. The table embodies the results of dilution found effective in this investigation.

‡ Dilution would depend on the normality of the solution, *e.g.*, 1000 cc. lime water of $N/25.5$ strength is required to coagulate 1 liter of latex, while only 10 cc. of 10 N-sodium hydroxide solution is effective.

† Minimum and maximum quantities of the bases were not determined, due to their immiscibility in water.

** Substances were not good coagulants in the concentrations used.

†† Coagulation studies embodied in this investigation were carried out mostly with latex having pH 4.6 and collected from Okhla plantations, Delhi, during the months of August and September, 1943, and it was noticed that seasonal variations of temperature and time exercise a great effect in bringing about coagulation. Low temperature of winter months has a retarding effect, while that of summer is favorable for it.

6. If the quantity of the coagulant exceeds the minimum amount required for the coagulation of latex, no coagulation occurs, and the latex passes into a second phase or zone.

7. When coagulation is effected by shaking, centrifuging, the application of dry heat, or adding alcohol and acetone, the pH value of the latex remains unchanged.

8. Coagulation is brought about also by reagents used for hydration and dehydration and for precipitating proteins, and by microörganisms and enzymes.

ACKNOWLEDGMENT

Our thanks are due to J. P. Anderson, Controller of Rubber, and H. R. Walden, Deputy Controller of Rubber and Officer-in-charge, Wild Rubber Section, Department of Supply, for the facilities and financial assistance for carrying out work on *Cryptostegia grandiflora* and other agricultural laticiferous plants to find substitutes for *Hevea brasiliensis*.

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II. EFFECT OF COAGULANTS ON THE QUALITY OF RUBBER *

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The present investigation is the outcome of the work described in Part I, which described results of coagulation of the latex of *Cryptostegia grandiflora* by chemical (acids, alkalies, salts) and miscellaneous reagents, water, heat, electric current, mechanical stirring, autocreaming and spontaneous or autocoagulation, and advanced some conclusions, but reserved explanation about coagulation for a future report.

The present communication adduces arguments concerning the phenomena of coagulation, and describes the effects and changes in rubber when it is obtained by coagulating the latex with various coagulants.

A sample of latex on coagulation gave dry rubber contents (D.R.C.) of 9.2–10.8 per cent, total solids, 18.4 per cent, and serum solubles, etc., 7.6 per cent. The coagula were analyzed for ash, total nitrogen, resins and rubber. They were then extracted with alcoholic potassium hydroxide and hydrochloric acid, and ash and nitrogen were again estimated in the unextracted residues. It was found that the coagula did not show any further appreciable loss of resins, proteins and inorganic components after acid and alkali treatment. It was also evident from observations that the composition of the rubber, except in coagula obtained by autocoagulation and cream (water), was more or less uniform, and did not vary with the coagulants. Detailed examination of resins extracted from rubber is in progress and will form part of a separate communication.

The latex of *Cryptostegia grandiflora* is a milky white emulsion of minute globules suspended in an aqueous serum of complex composition, while coagulation is a process of deëmulsification and resolution of latex into a coagulum and serum by agencies which may be physical and chemical. The coagulum formed by the fusion of rubber with resins, proteins, and inorganic components has a spongy mesh work, and is filled with serum, but after its removal on pressing becomes tough, tenacious and elastic. It has not been possible to obtain a coagulum consisting of pure rubber hydrocarbon by coagulants described in this investigation.

Various theories have been advanced at times to explain the phenomena of coagulation. One postulates the phenomena to be due to the removal of protein[1] or resin films[2]. Coagulation is attributed by some to the action of enzymes[3] or bacterial activity[4], while Gardner considers it a purely physical phenomenon caused by disturbance of the physical equilibrium of the latex[5]. According to Kruyt[6], latex is a lyophilic colloid of feeble solvation, whose stability can be modified by electric charge and the solvation. "The particles of rubber carry a negative charge, and if this be neutralized by the addition of acid or metallic ions, solvation alone would be insufficient to assure stability of the system. In the same way, if in a latex of lightly charged particles the feeble solvation is nevertheless sufficient to produce stability, coagulation results if the solvation be reduced by addition of dehydrating agent, *e.g.*, alcohol or a concentrated solution of caustic alkali."[7]

Our own observations show that coagulation of the latex of *Cryptostegia grandiflora* is brought about: (1) by agents which coagulate proteins and which

* Reprinted from the *Journal of the Indian Chemical Society*, Vol. 21, No. 6, pages 215–221, June 1944.

neutralize the charge on rubber particles, (2) by hydration (water) and dehydration (anhydrous sodium sulfate, potassium carbonate, caustic alkali and alcohol), (3) by autocoagulation (enzymes and bacterial activity), (4) by shaking, centrifuging, when the pH remains unaltered, (5) by smoking, heat, electric current, etc.

The data show further that the rubber particles carry a negative charge, and that resins and proteins are not completely removed from the rubber, but a portion remains adsorbed on it, while another is eliminated during the process and is probably of a different nature. These observations lead us to share the views expressed by Kruyt, and we believe that coagulation is brought about by profound changes produced by physical and chemical agencies which destroy the stability of the system by partial or complete elimination of resins, proteins and serum components, neutralization of the charge on the rubber, and its separation as coagulum, and by the disruption of electrical, molecular and cohesive forces that pervade the latex of *Cryptostegia grandiflora*. We visualize a molecule of latex[8] as composed of a central core of rubber suspended in a stout bag of resins filled with serum, and this bag is further enclosed in another bag made of protein substances, with the intervening space filled with serum. Internal changes due to enzymes, etc., or external changes to chemical or physical agencies, make a puncture in the bags, whereby serum oozes out, and the sac walls collapse and fuse with rubber. On account of their lightness, these fused particles tend to rise to the surface of serum to form a dense layer of cream and, by further fusion and coalescence of these cream particles, a spongy coagulum is produced during coagulation. Failure of coagulation or stabilization of latex under certain conditions or at certain periods of its metabolism is probably due to an increase in tone and resistance of the films associated with rubber, and the concentration of coagulants is not enough to overcome their protective action.

EXPERIMENTAL

A sample of latex obtained, in the month of October 1943, from Oakhla (Delhi) plantations, having pH 4.6, was coagulated with various coagulants, as shown in Table I. For each coagulation 50 cc. of latex was used, and a coagulum was immediately obtained when alcohol, acetone, water, steam, sodium hydroxide were used as coagulants, whereas with picric, acetic and mineral acids and salt solutions the latex after mixing with the coagulant was kept overnight, whereupon it thickened and, on warming and stirring with a glass rod for 2–10 minutes, the flocks separated and soon coalesced to a spongy white coagulum. In each case after pressing and washing with water, the coagulum was kept under water for two days. It was next kept in boiling water for half an hour. All the coagula were dried in an air-oven at 90°. When coagulation was effected with pyridine, alcohol and sodium hydroxide, two volumes of latex were used. One coagulum from pyridine and sodium hydroxide was washed with water alone, the other was dipped in 10 per cent acetic acid before washing. They are shown in Table I as "pyridine (water), pyridine (acid), sodium hydroxide (water), sodium hydroxide (acid)". From the alcohol coagulation one coagulum was removed at once from the serum, while the other was allowed to remain in it overnight. These are shown in the table as "alcohol I and alcohol II". The serum was in some cases turbid. That from alcohol was analyzed for nitrogen, and gave a value of 10.47 per cent (65.63 per cent as protein). Besides, one coagulum was obtained by centrifuging and

another by spontaneous or autocoagulation, while the whole latex was secured by completely drying the latex to a constant weight at 90°. The total solids of one experiment are shown as cream (water). To obtain them, latex (50 cc.) was diluted with water (200 cc.), whereby flocks separated, which, after removing from serum, were dried at 90°.

TABLE I

PERCENTAGE OF D.R.C. OBTAINED BY COAGULATING LATEX WITH VARIOUS COAGULANTS

No.	Name of coagulant	Coagulant in cc. or g.	Dilution with water	Serum	pH	Percentage D.R.C. on volume basis
1	Alcohol I	50 cc.	—	Brownish with suspension	4.6	9.22
2	Alcohol II	50 cc.	—	Brownish with suspension	4.6	10.07
3	Acetone	50 cc.	—	Brownish with suspension	4.6	10.86
4	Picric acid	0.05 g.	5 cc.	Yellow and turbid	—	10.34
5	Pyridine (water)	0.025 cc.	5 cc.	Slightly dark and turbid	5.0	10.50
6	Pyridine (acid)	0.025 cc.	5 cc.	Slightly dark and turbid	5.0	10.31
7	Sodium hydroxide (water)	*N* soln.	5 cc.	Slightly dark and turbid	—	10.23
8	Sodium hydroxide (acid)	*N* soln.	5 cc.	Slightly dark and turbid	—	9.77
9	Acetic acid	0.25% soln.	5 cc.	Slightly dark and turbid	4.2	10.37
10	Sulfuric acid	0.1% soln.	5 cc.	Slightly dark and turbid	4.2	10.19
11	Nitric acid	0.1% soln.	5 cc.	Slightly dark and turbid	4.2	10.27
12	Hydrochloric acid	0.25% soln.	5 cc.	Slightly dark and turbid	4.2	10.36
13	Sodium chloride	0.05% soln.	5 cc.	Slightly dark and turbid	4.5	9.83
14	Ammonium sulfate	0.05% soln.	5 cc.	Slightly dark and turbid	4.4	10.26
15	Alum (potash)	0.05% soln.	5 cc.	Brownish and turbid	4.5	10.62
16	Calcium chloride	0.05% soln.	5 cc.	Brownish and turbid	4.4	10.42
17	Aluminum sulfate	0.05% soln.	5 cc.	Slightly dark and turbid	4.4	10.44
18	Potassium sulfate (anhyd.)	5 g. soln.	5 cc.	Slightly dark and turbid	4.5	10.43
19	Water (to complete coagulation)	—	—	Clear, straw colored	—	9.80
20	Steam (till 130 cc. condensed)	—	—	—	—	10.11
21	Cream (water)	—	200 cc.	Straw colored	—	10.20
22	Centrifuge (till coagulum separated)	—	—	Turbid	—	10.60
23	Autocoagulation	—	—	Straw colored	4.2	10.80
24	Whole latex	—	—	—	—	18.36*

* Total solids are on the weight of latex.

The results given in Table I confirm our previous findings, and show that there is not much difference in the percentages of coagula obtained by coagulating the latex with various coagulants. They range between 9.2–10.8, and thus show a slight variation of 1.6 per cent, part of which may be due to sampling, as it is difficult to maintain the uniformity of the sample. The total solids amount to 18.4 per cent and the serum solubles or otherwise give a figure of 7.6 per cent.

Under conditions where the maximum difference in the percentages of coagula is 1.6, the water coagulation method seems to be the best, since it does not require chemicals or keeping the latex overnight. The only difficulty in the process is that big coagulating pans would be necessary, but to overcome this cemented tanks of suitable size, depending on the daily supply of latex, with an exit at the bottom, should serve the purpose.

To find the quality of rubber, the coagula were analyzed for ash, nitrogen and resins, and rubber was calculated by difference. Table II embodies the results and percentage composition of coagula on the basis of D.R.C. and latex. Their ash contents were determined by heating them slowly and carefully in a platinum dish. Catching fire of combustible products was avoided. The material charred, and finally a white ash was obtained. The nitrogen was determined by the Kjeldahl method, and to obtain a value for protein the percentage was multiplied by the factor 6.25. For the determination of resins, coagula (not less than 1 gram) were extracted with alcohol four times (25 cc.

TABLE II

COMPOSITION OF COAGULA

No.	Coagula from	Percentage composition of coagula					Percentage composition of coagula on latex						Percentage of substances removed with serum
		Ash	Nitrogen	Protein	Resins	Rubber	Moisture	Ash	Nitrogen	Protein	Resins	Rubber	
1	Alcohol I	0.73	0.59	3.69	13.52	82.06	81.64	0.07	0.05	0.34	1.25	7.57	9.14
2	Alcohol II	0.84	0.69	4.29	13.37	81.50	81.64	0.08	0.08	0.43	1.35	8.21	8.29
3	Acetone	1.19	0.52	3.25	13.93	81.63	81.64	0.12	0.05	0.35	1.41	8.86	7.62
4	Picric acid	0.39	0.72	4.49	15.52	79.60	81.64	0.04	0.07	0.46	1.60	8.23	8.02
5	Pyridine (water)	0.39	0.68	4.23	14.29	81.09	81.64	0.04	0.07	0.44	1.50	8.51	8.61
6	Pyridine (acid)	0.14	0.68	4.26	13.40	82.28	81.64	0.01	0.07	0.44	1.38	8.47	8.05
7	Sodium hydroxide (water)	1.30	0.35	2.21	15.14	81.35	81.64	0.13	0.04	0.23	1.55	8.32	8.13
8	Sodium hydroxide (acid)	0.44	0.40	2.28	14.66	82.62	81.64	0.04	0.04	0.22	1.43	8.07	8.52
9	Acetic acid	0.25	0.58	3.64	13.39	82.72	81.64	0.03	0.06	0.38	1.39	8.57	8.00
10	Sulfuric acid	0.22	0.74	4.60	13.66	81.52	81.64	0.02	0.08	0.47	1.39	8.30	8.18
11	Nitric acid	0.18	0.64	4.01	13.99	81.82	81.64	0.02	0.07	0.41	1.44	8.39	8.10
12	Hydrochloric acid	0.35	0.76	4.74	14.12	80.79	81.64	0.04	0.08	0.49	1.46	8.29	8.08
13	Sodium chloride	0.30	0.55	3.45	13.55	82.70	81.64	0.03	0.06	0.40	1.33	8.13	8.53
14	Ammonium sulfate	0.71	0.65	4.04	12.59	82.66	81.64	0.07	0.07	0.41	1.29	8.47	8.11
15	Alum (potash)	0.33	0.61	3.79	12.79	83.09	81.64	0.03	0.06	0.40	1.38	8.81	7.76
16	Calcium chloride	0.32	0.54	3.39	15.10	81.19	81.64	0.03	0.06	0.35	1.57	8.46	7.94
17	Aluminum sulfate	0.68	0.78	4.79	14.62	79.91	81.64	0.07	0.08	0.50	1.93	8.34	7.93
18	Sodium sulfate (anhyd.)	0.69	0.74	4.60	15.70	79.01	81.64	0.07	0.08	0.48	1.64	8.24	7.93
19	Water	0.30	0.60	3.72	14.19	81.79	81.64	0.03	0.06	0.37	1.39	8.04	8.55
20	Steam	0.52	0.77	4.77	13.55	81.16	81.64	0.05	0.08	0.48	1.37	8.20	8.26
21	Cream (water)	0.81	1.24	7.74	18.28	73.17	81.64	0.08	0.13	0.79	1.86	7.46	8.16
22	Centrifuge	1.16	0.78	4.90	14.20	79.75	81.64	0.13	0.09	0.53	1.55	8.68	7.47
23	Autocoagulation	0.56	1.34	8.34	17.74	73.36	81.64	0.06	0.14	0.90	1.92	7.92	7.56
24	Whole latex*	3.55	2.12	13.26	36.31	46.88	81.64	0.65	0.29	2.43	6.67	8.61	—

* Moisture has been assumed on the basis of loss suffered by latex on drying at 90°.

each time) on a water-bath for 20 hours. The alcoholic extract of coagula, except that of whole latex and cream (water), was concentrated and, on keeping at room temperature, deposited a white substance, which contained 0.916 per cent of nitrogen (5.73 per cent as protein). The filtrate on removal of the solvent from this substance gave an ether-soluble oily residue (3.2516 grams) with a nitrogen content of 0.485 per cent, while the ether-insoluble fraction was further resolved into water-soluble (0.0524 gram) having nitrogen 0.895 per cent and water-insoluble (0.1 gram) with 1.964 per cent nitrogen.

The foregoing table shows a high percentage of ash in coagula obtained from alcohol, acetone, sodium hydroxide, alum, and ammonium and sodium sulfates, and still higher in cream (water), centrifuge, autocoagulation and whole latex, but less in coagula from acid coagulants or those which were dipped in acid solutions before washing. Thus the ash content of the total solids (whole latex) was 3.56 per cent (0.66 per cent on latex), while those of other coagula depended on a coagulant. No generalization can be made except that, by coagulation, ash-free rubber is not possible and that a greater portion of the inorganic components is removed by serum and washing. The total nitrogen on the weight of whole latex was 2.12 per cent (13.26 per cent, calculated as proteins and 0.39 per cent as nitrogen and 2.12 per cent as protein on the weight of latex). The coagula from autocoagulation and cream (water) showed nitrogen 1.335 and 1.230 per cent (8.34, 7.74 per cent as protein), respectively. These values are higher than those obtained for other coagula, which ranged from 0.35–0.77 per cent (2.2–4.8 per cent as protein). From the data it is evident that part of the nitrogen is serum-soluble (14.9 per cent as protein) and partly insoluble (8.3 per cent as protein), and removal of a portion (3.5–6.1 per cent as protein) from this depends on the coagulants. Turbidity of the serum in some cases and the analytical results of the turbid mass obtained from serum after coagulating the latex with alcohol further supports this viewpoint. The observed value for nitrogen was 10.47 per cent (65.6 per cent as protein). However, all the nitrogen cannot be proteinous, and a considerable portion of it contained in the latex is removed during coagulation, but 3–4 per cent, in spite of washings, goes into the meshwork structure of the coagula, and probably continues to form shells surrounding the rubber particles. Comparative vulcanization studies of whole latex and of coagula produced by autocoagulation, water, acids, alkalies will explain the role of proteins in rubber.

The whole latex contained 36.31 per cent alcohol solubles (resins) (6.7 per cent on latex) while the total solids from cream (water) and coagulum from autocoagulation contained 18.3 and 17.7 per cent, respectively. In other coagula the alcohol-solubles ranged between 12.6–15.7 per cent. Thus more than one-half of the resins are serum-soluble, and seem to be different from those which remain adsorbed on rubber by the formation of protective films which are not removed at pH values of 4.6–4.2. Rubber is calculated by difference. The table shows further that, in the total solids of *Cryptostegia grandiflora*, resins, proteins and inorganic components which remain adsorbed on the rubber amount to 1/5, 1/7, 1/6, respectively, of those originally present in the latex.

It appeared, however, necessary to find out whether the rubber hydrocarbon contents of coagula would show any further variation of percentage on extraction with alcoholic potassium hydroxide and alcoholic hydrochloric acid solutions.

Extraction of the Coagula with Alcoholic Potassium Hydroxide and Alcoholic Hydrochloric Acid Solutions.—The coagula were divided into two groups, A

and B. Group A comprised twelve coagula, while there were eleven in group B, and were kept separate. The extraction was carried out with 0.5 *N* alcoholic potassium hydroxide solution (100 cc. for Group A and 25 cc. for each of the coagula of Group B). The solution was prepared by dissolving potassium hydroxide (30 g.) in water (30 cc.), and diluting the solution with alcohol (1000 cc.) on the water-bath for six hours. The coagula were washed with alcohol and finally with water (twice) by warming on a water-bath for 6 hours. They were dried at 90° in an air oven and then *in vacuo* over sulfuric acid.

TABLE III

DISTRIBUTION OF ASH AND NITROGEN IN COAGULA AND THEIR LOSSES ON EXTRACTION WITH EtOH-KOH AND EtOH-HCl SOLUTIONS

	Coagula from Group A	Loss after alc. KOH extn. (%)	Loss after alc. HCl extn. (%)	N after alc. extn. (%)	N after alc. KOH extn. (%)	N after alc. HCl extn. (%)	Ash after alc. extn. (%)	Ash after alc. KOH extn. (%)	Ash after alc. KCl extn. (%)	Increase in ash after HCl extn. (%)
	Alcohol I, II, acetone, pyridine (water), (acid), sodium chloride, acetic, sulfuric, nitric, hydrochloric acids, ammonium sulfate and alum (potash)	1.14	0.64 inc.	0.47 (average of 12 samples)	0.60	0.62	0.64 (average of 12 samples)	0.79	0.71	
No.	Group B									
1	Calcium chloride	2.04	0.39 inc.	0.54	Not det.	0.49	0.32	Not det.	0.57	0.25
2	Aluminum sulfate	0.81	0.42 inc.	0.78	Not det.	0.82	0.68	Not det.	0.91	0.23
3	Sodium sulfate	3.57	No loss	0.74	Not det.	0.43	0.69	Not det.	1.17	0.48
4	Picric acid	0.12	0.35 inc.	0.72	Not det.	0.39	0.39	Not det.	0.80	0.41
5	Sodium hydroxide (water)	1.64	0.33 inc.	0.36	Not det.	0.43	1.30	Not det.	1.25	—
6	Sodium hydroxide (acid)	0.07	0.23 dec.	0.40	Not det.	0.32	0.44	Not det.	0.76	0.32
7	Water	0.07	0.24 inc.	0.60	Not det.	0.43	0.30	Not det.	0.99	0.69
8	Steam	1.17	0.13 inc.	0.77	Not det.	0.74	0.52	Not det.	0.85	0.35
9	Cream (water)	2.32	2.34 inc.	1.24	Not det.	0.67	0.81	Not det.	1.26	0.45
10	Autocoagulation	3.74	0.36 dec.	1.34	Not det.	1.02	0.56	Not det.	0.53	—
11	Whole latex	10.38	0.33 dec.	2.12	Not det.	0.17	3.55	Not det.	0.86	—

Nitrogen and ash were determined only for the coagula of Group A, and the coagula of both the groups were next extracted with 0.5 per cent alcoholic hydrochloric acid for six hours (30 cc. for each sample of Group B and 150 cc. for Group A). The coagula were washed with alcohol and finally with water, and were dried as in the previous case. There was no loss of any significance by this treatment. There was a slight increase or decrease in weight. The coagula after extraction with potassium hydroxide solution showed losses which were more in those obtained from cream, steam and autocoagulation, while whole latex showed a loss of 10.4 per cent. The losses are due to the elimination of inorganic substances and proteins, etc., as supported by data in Table III. The ash and nitrogen were determined in all the coagula of Groups A and B after their extraction with alcoholic hydrochloric acid, and they required more sulfuric acid for digestion than was ordinarily required in Kjeldahl estimations of nitrogen.

The foregoing table shows the course of nitrogen and ash in coagula after various treatments. In some cases there is an increase in the ash content, and this corresponds with their increase in weight after alcoholic acid extraction. It is possible that some potassium hydroxide remained in rubber, and combined with hydrochloric acid and the resultant potassium chloride adsorbed on rubber.

CONCLUSIONS

1. Whatever coagulant is used for coagulation, a certain proportion of inorganic components, proteins and resins (1/9, 1/7, 1/5, respectively) of those originally present in latex remains adsorbed on rubber.

2. One-half of the total solids are eliminated with serum during coagulation.

3. The quality of rubber does not vary with a coagulant.

4. The molecules of latex[8] are saclike bodies consisting of an inner core of rubber surrounded by protective films of resins and proteins, and the intervening spaces are filled with serum components. A puncture in the latex sac expels the serum components and brings about a collapse of the protective films which get adsorbed on rubber and these fused sacs float in serum as cream. By further fusion of cream particles a spongy coagulum of rubber is formed.

5. Coagulation is brought about because of profound changes in latex produced by physical and chemical agencies which destroy the stability of the system by elimination of resins, proteins and serum components, by neutralization of the charge on the rubber, and by the disruption of electrical, molecular and cohesive forces that pervade latex.

ACKNOWLEDGMENT

Our thanks are due to J. P. Anderson, Controller of Rubber, and H. R. Walden, Deputy Controller of Rubber, for the facilities during this investigation.

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[8] It is not quite clear whether the expression "molecules of latex" should be understood to mean "latex particles" or "rubber molecules which as aggregates constitute a latex particle".

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RUBBER CHEMISTRY AND TECHNOLOGY

VOLUME XVIII NUMBER 4

October, 1945

Published Quarterly under the Auspices of the
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of the
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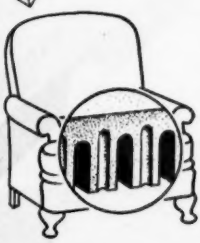

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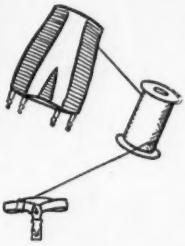

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SHARPLES RUBBER CHEMICALS

VULCANIZING AGENTS	PLASTICIZERS	SOLVENTS FOR GR-S	BASIC CHEMICALS FOR RUBBER COMPOUNDING MATERIALS
VULTAC* NO. 1	Pentalenes †	Dichloropentanes	Ethylamines, Butylamines, Amylamines, Ethylethanolamines, Diethylaminoethanol, Butylethanolamines, Dibutylaminoethanol.
VULTAC* NO. 2	Dialkyl Acid Amides ‡	Mixed Amyl Chlorides	*Also other alkyl and alkylalkylolamines available in experimental quantities.*
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* Trade Name Registered. Chemically the VULTACS are alkylphenol sulfides.

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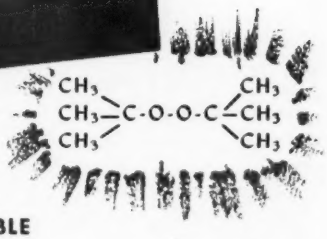

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Index of Refraction	$n_D^{25^\circ}$ 1.3874
Boiling Point	107.5°–109.5° C
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1. Appears to be especially useful in high temperature and pressure polymerizations.
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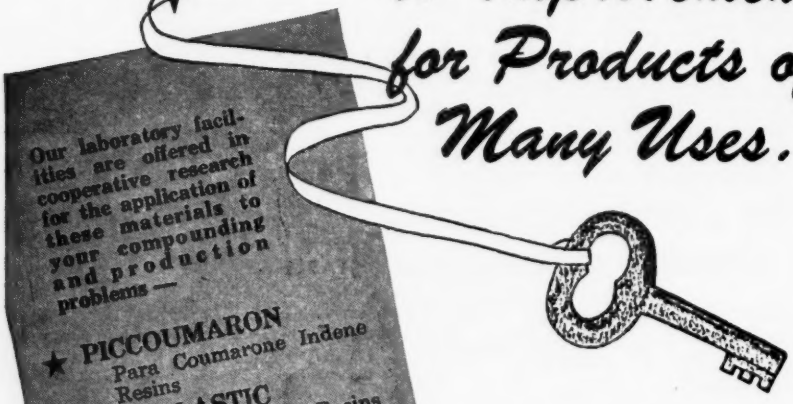

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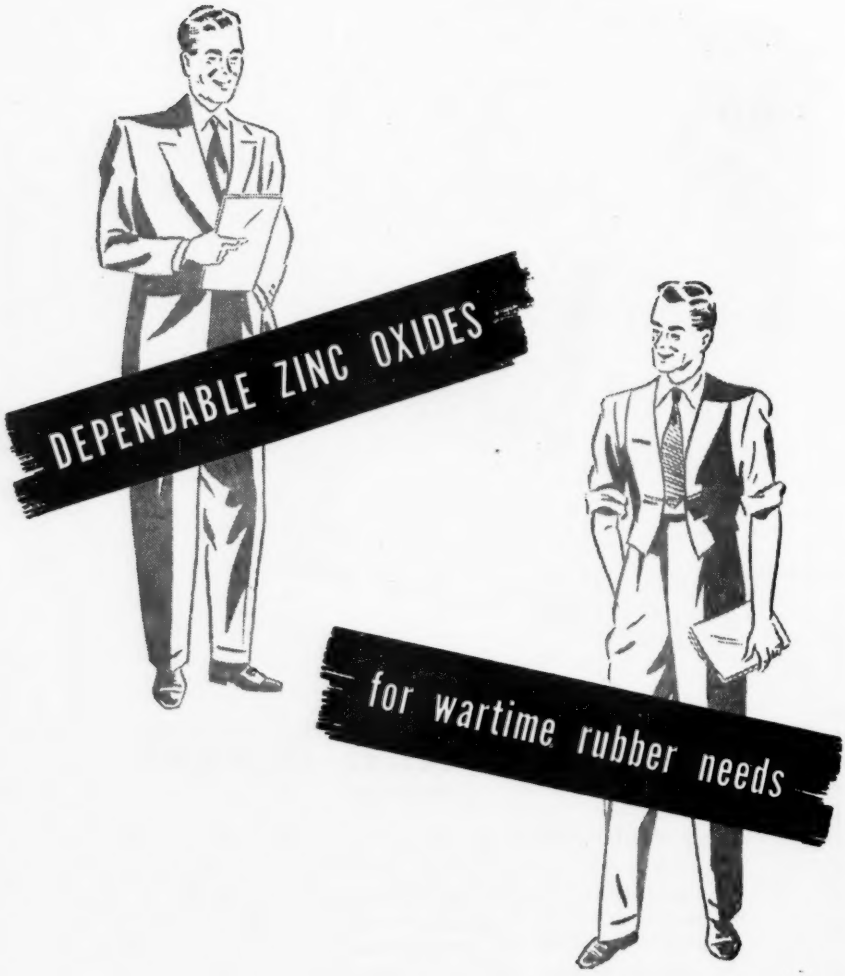

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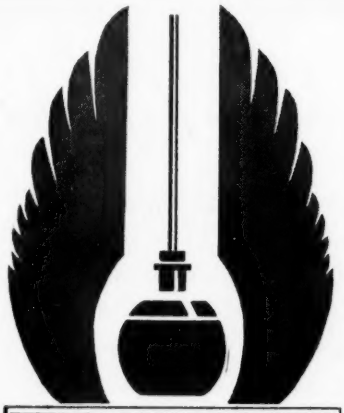

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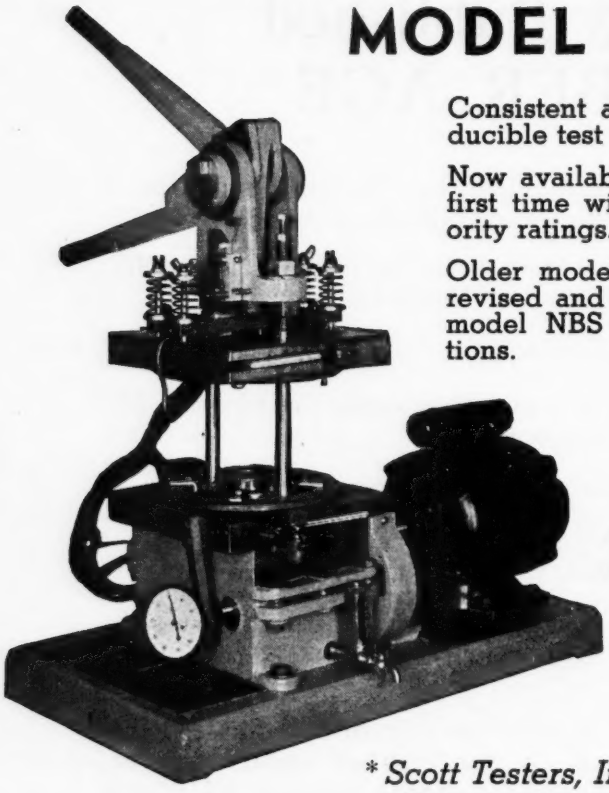

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Dibutyl Phthalate	30.0
Protective Wax*	2.0
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Original	1700	790	470	45	
Oven Aging 70 hrs. @ 212°F	1770	560		50	
Immersion ASTM Test Oil Number 3, 70 hrs. @ 212°F	1540	600		45	+3.
Immersion in 40% Aromatic Test Fluid SR-6 168 hrs. at room temperature	900	460		29	+34.
Immersion in Gasoline Test Fluid SR-10 168 hrs. at room temperature	1600	730		40	—0.5

Compression Set ASTM Method B	22 hrs. @ 158°F	23 per cent
	70 hrs. @ 212°F	66 per cent
Rebound (Goodyear-Healy)	@ 104°F	61 per cent
	@ 212°F	69 per cent
Tear Test ASTM D 624-44 @ Room Temperature		240 pounds per inch
Low Temperature Brittleness D 736-43T		O.K. at—55°F

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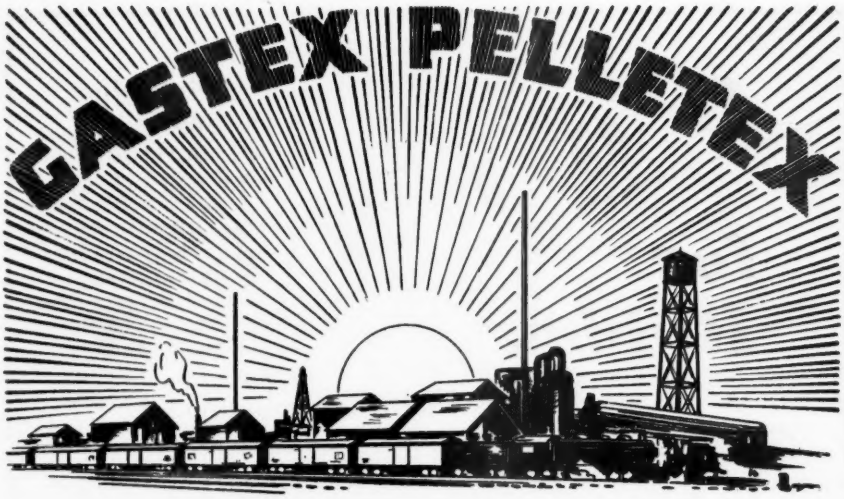

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A-19

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DIOCTYL and DIBENZYL SEBACATES

PLASTICIZERS 35 and 36

POLYMERIC OR RESINOUS TYPES

PARAPLEX G-25

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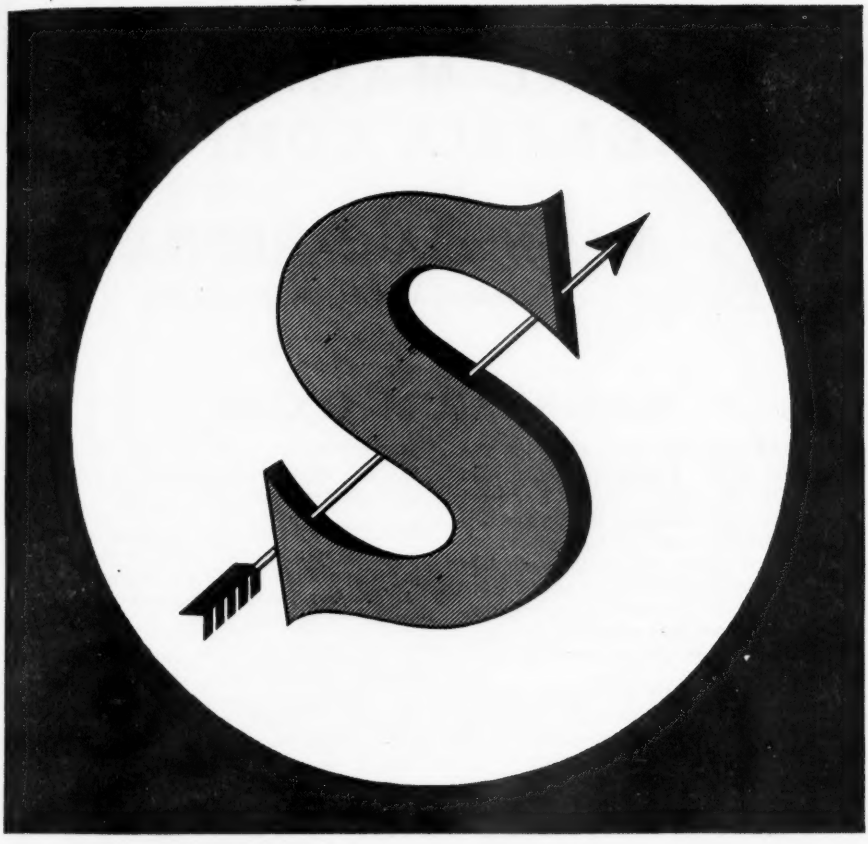

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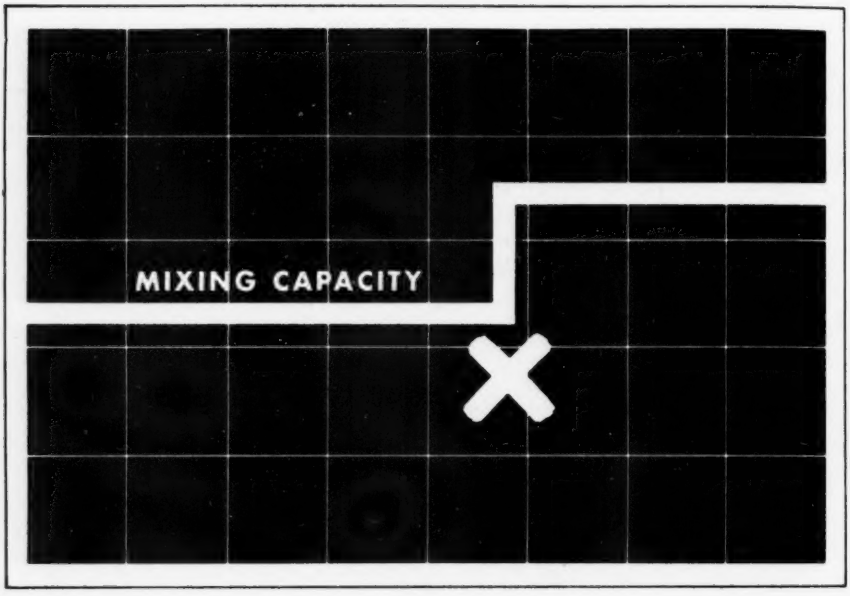

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